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Sorption of
2,4-Dichlorophenol and 2,4,5-Trichlorophenol
by Softwood Fibers

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SORPTION OF 2,4-DICHLOROPHENOL AND 2,4,5-TRICHLOROPHENOL BY SOFTWOOD FIBERS

A Thesis Submitted by

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ABSTRACT

Batch sorption experiments for the retention of 2,4-dichlorophenol and 2,4,5-trichlorophenol by pulped wood fibers indicate that sorption is governed by the interaction of the acid form of these compounds with lignin. Measurements of fiber-water distribution coefficients over a pH range of 2 to 12 demonstrate that chlorophenolate ions do not sorb to the solid phase, and the interaction between the neutral form of the compound and lignin is primarily responsible for the retention within this pH region. This was confirmed by experiments using lignin and cellulose model particles and pulp fibers of various lignin content. The results have led to the development of an equation which relates the overall fiber-water distribution coefficient to the ionization of the phenol, the lignin mass fraction of the fiber, and a lignin-water distribution coefficient which can be estimated with a linear free-energy relationship.

Modeling the fiber-water transfer of chlorophenols, as a distribution process between water and lignin phases, was successful in the treatment of concentration, temperature, and inorganic salt effects. Sorption isotherms were shown to be linear and have no dependency on phenolic cosolutes at concentration levels common in bleaching effluents. Distribution coefficients demonstrated only a small dependency on temperature and inorganic salt concentrations which could be predicted from the solute's heat of aqueous dissolution and Setschenow constants, respectively. A thermodynamically consistent collisional desorption model was developed for the solids concentration effect, but the fiber system demonstrated no dependency on sorbent levels. Other results include a dependency of sorption on colloidal or "third-phase" concentrations and no dependency of sorption on fiber surface area.

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C_s	Solid Phase Concentration of Solute
C_w	Aqueous Phase Concentration of Solute
K_f	Freundlich Constant
n	Sorption Intensity Constant for Freundlich Model
K_d	Solid-Water Distribution Coefficient
χ_s	Fraction of Solute Sorbed to Solid Phase
V	Total Volume of Aqueous Solution
m_s	Mass of Solids in Aqueous Phase
S	Solids Concentration
f_{om}	Mass Fraction of Organic Material in Soils and Sediments
K_{om}	Organic-Water Distribution Coefficient for Soils and Sediments
f_{min}	Mass Fraction of Mineral Material in Soils and Sediments
K_{min}	Mineral-Water Distribution Coefficient for Soils and Sediments
$\mathcal{F}_{om}$	Fugacity for Solutes in Organic Phase of Soils and Sediments
$\mathcal{F}_w$	Fugacity for Solutes in Aqueous Solution
χ_{om}	Mole Fraction of Solute in Organic Phase of Soils and Sediments
γ_{om}	Activity Coefficient for Solute in Organic Phase of Soils and Sediments
χ_w	Mole Fraction of Solute in Aqueous Phase
γ_w	Activity Coefficient for Solute in Aqueous Phase
K_p	Partition Coefficient
$\overline{V}_w$	Molar Volume of Water
$\overline{V}_{om}$	Molar Volume of Organic Phase in Soils and Sediments
ρ_{om}	Density of Organic Phase in Soils and Sediments
g^E	Excess Free Energy

$\triangle G^E_{om}$	Molar Excess Free Energy of Transfer for Sorption to Soils and Sediments
$\triangle G_{om}$	Free Energy of Transfer for Sorption to Soils and Sediments
g^x_{om}	Change in Free Energy of Transfer for Sorption to Soils and Sediments
K_{ow}	Octanol-Water Distribution Coefficient
$\triangle G^E_{ow}$	Free Energy of Transfer for Octanol-Water Transfer
g^x_{ow}	Change in Free Energy of Transfer for Octanol-Water Transfer
a	Parameter of LFER
b	Parameter of LFER
CPM	Counts per Minute
DPM	Disintegrations per Minute
E	Counting Efficiency
m_f	Mass of Fiber in Sorption Sample
V_s	Volume of Filtrate Sampled in Sorption Studies
m_l	Mass of Lignin in Sorption Sample
s_c	Mass of Solute Retained by Cellulose
s_l	Mass of Solute Retained by Lignin
s_w	Mass of Solute Retained in Water Held by Fibers
$m_{o.d.}$	Oven-dried Mass of Fiber in Sorption Sample
f_c	Mass Fraction of Cellulose in Fiber
C_c	Concentration of Solute Retained by Cellulose
f_l	Mass Fraction of Lignin in Fiber
C_l	Concentration of Solute Retained by Lignin
K_c	Cellulose-Water Distribution Coefficient
K_l	Lignin-Water Distribution Coefficient

V_{fw}	Volume Water Retained by Fibers
C_f	Consistency of Fibers
ρ	Density of Aqueous Solution
k_w	Water Retention Coefficient
η	Kappa Number
α	Fraction of Compound in Neutral Form
K_d^0	Fiber-Water Distribution Coefficient for Neutral Compound
pH	pH of Aqueous Solution
pK_a	Acid Dissociation Constant of Solute
K_c^0	Cellulose-Water Distribution Coefficient for Neutral Compound
K_l^0	Lignin-Water Distribution Coefficient for Neutral Compound
γ_l	Activity Coefficient of Solute in Lignin Phase
$\overline{V}_l$	Molar Volume of Lignin
ρ_l	Density of Lignin
$\triangle H_s^E$	Heat of Aqueous Dissolution
$\triangle H_{sorp}$	Heat of Sorption
γ_w^{salt}	Aqueous Activity Coefficient at Elevated Inorganic Salt Levels
K^s	Setschenow Constant
$[salt]$	Molar Concentration of Inorganic Salt
K_d^{salt}	Fiber-Water Distribution Coefficient at Elevated Inorganic Salt Levels
k_1	Sorption Rate Constant
k_2	Desorption Rate Constant
t	Time
$[SP]$	Concentration of Reversibly Sorbed Solute

$[S]$	Aqueous Concentration of Solute
$[P]$	Aqueous Concentration of Sorbent
$[SP]_0$	Concentration of Reversibly Sorbed Solute at Initial Time
$[S]_0$	Aqueous Concentration of Solute at Initial Time
$[S]_T$	Total Concentration of Solute
$[P]_0$	Aqueous Concentration of Sorbent at Initial Time
k'	Defined Rate Constant
f	Fraction of Solute Remaining on Particle after Collision
τ	Time Period between Collisions
K	Reversible Partition Coefficient
K^0	Conventional Partition Coefficient
f_{trans}	Kinetic Energy Transferred
m_1	Mass of Colliding Particle
m_2	Mass of Colliding Particle
k_3	DiToro's Collision-Induced Desorption Rate Constant
C	Collision Factor
$K_d^{apparent}$	Fiber-Water Distribution Coefficient at Elevated Colloidal Levels
r_{cw}	Aqueous Concentration of Colloidal Material
K_{cw}	Colloid-Water Distribution Coefficient
C_w^{eq}	Equilibrium Aqueous Phase Concentration of Solute

BACKGROUND AND THESIS OBJECTIVES

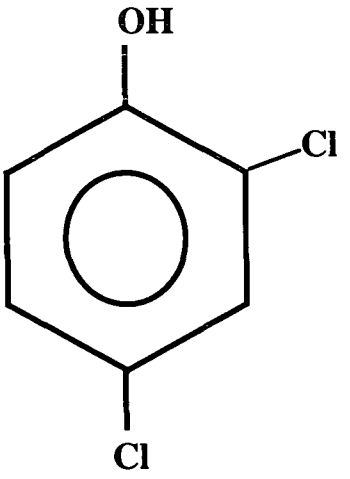
INTRODUCTION

This project studies the distribution of organic chemicals between an aqueous solution and pulp-derived solids. This is a process which is important in many areas of the pulp and paper industry, but here the emphasis is on the retention of chloroorganic materials by primary sludge. The two model compounds studied (Table 1) demonstrate properties common to several materials found in bleaching effluents; both are hydrophobic in nature but possess polar and ionizable groups.[1-10] Variables important to the distribution process include the organic and inorganic composition, temperature, and solids concentration of effluents, and the chemical composition of fibrous solids in sludge. The goal of this research was the development of predictive equations which take these variables into account. The literature on the organic sorption to pulp-derived substrates is scarce, but there does exist a significant amount of information on the aqueous sorption of organic chemicals to other organic sorbents including chromatographic materials,[11-16] soils and sediments,[17-22] and biophases.[23-26] The modeling of sorption in these systems provides an excellent guide for predicting the distribution of organics between water and organic solids.

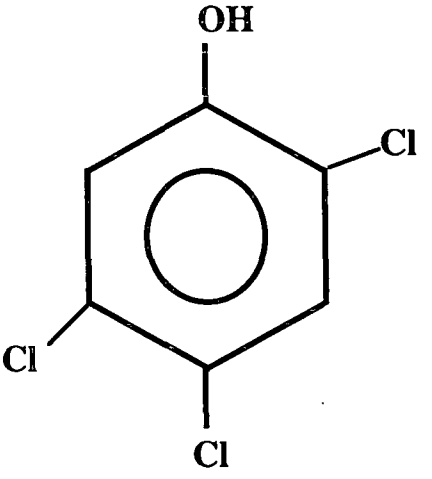
The purpose of this chapter is to provide general background information on the solid-water distribution of organic chemicals. This will include a discussion on quantifying sorption, a thermodynamic description of the process, and a brief introduction to linear free-energy relationships. Details on the role of other variables will be presented as part of the introduction in each of the chapters which follow. Reference will be made primarily to sorption studies using soils or sediments. These materials

are similar to pulped wood fibers in that both have a complex structure composed of hydrophilic and hydrophobic chemical fractions. For soils and sediments, it is the hydrophobic organic fraction that dominates the retention of aqueous nonpolar chemicals. In water, this organic material, which is composed of chemicals such as proteins, lignin, and cellulose, is believed to exist as nonpolar pockets which sparsely populate mineral surfaces. Modeling efforts treat these regions as a nonpolar "pseudophase" into which hydrophobic solutes can partition in a process similar to the distribution of an organic solute between water and an organic solvent.[27]

Table 1. Structural formulas of 2,4-dichlorophenol and 2,4,5-trichlorophenol.



2,4-Dichlorophenol



2,4,5-Trichlorophenol

THE SOLID-WATER DISTRIBUTION OF ORGANIC CHEMICALS

Sorption Isotherms and the Solid-Water Distribution Coefficient

For measurements of the distribution of an organic solute between an aqueous solution and a solid phase, results are commonly expressed as sorption isotherms. A sorption isotherm is a plot of the equilibrium concentration of the compound bound to the solid phase, C_s(mol· mL^{-1}), vs. the concentration of the compound remaining in the water phase, C_w(mol· g^{-1}). Isotherms for the sorption of organics to naturally occurring solids can typically be fit with a Freundlich model. The Freunlich isotherm, as opposed to a Langmuir isotherm for example, does not become linear at low solute concentrations, nor does it reach a saturation level. Instead, the isotherm continuously changes at a constant rate with solute concentration. The Freundlich model can be shown to be thermodynamically rigorous for special cases of sorption on heterogeneous surfaces, but its origins and applications are for the most part empirical. The model has the general form

$$C_s = K_f C_w^n \tag{1}$$

The parameter K_f (i.e., Freundlich constant) is related to sorption capacity and n to sorption intensity (Fig. 1). The shape of an isotherm is often rationalized qualitatively by a proposed mechanism. A nonlinear isotherm is usually associated with adsorption resulting from either competition between solutes for depleting binding sites ($n < 1$) or enhancement of the surface for further sorption by retained solutes ($n > 1$). Linear isotherms ($n = 1$) are associated with an absorption process where the increasing

solute concentration has little impact the distribution ratio between the two phases. Although these connections between isotherm shapes and sorption mechanism appear quite clear, measurements in environmental systems are often variable due to low solute concentrations and the heterogeneous nature of substrates. This can result in the loss of detail, which would indicate subtle upward or downward trends in isotherms. Also, an isotherm fit may be tied to a certain concentration region. For example, at low solute concentrations, isotherms can often be fit with a linear model ($n = 1$)[20,27]; at higher levels, a nonlinear model ($n \neq 1$). Thus, the assignment of mechanism based on isotherm shape is a rather tenuous practice.

For modeling purposes, a linear model fit within the concentration region of interest is desirable because it allows the sorption process to be described by a constant, the ratio between the solute's concentration in the solid, C_s, and water, C_w, phases

$$K_d = \frac{C_s\ (mol \cdot g^{-1})}{C_w\ (mol \cdot mL^{-1})} \tag{2}$$

This ratio is often referred to as the distribution coefficient, K_d ($K_d = K_f$, when $n = 1$), which is commonly used to model the transport of a solute in environmental systems. K_d can be thought of as a measure of the ability of a solid material to concentrate a chemical. The fraction of total solute mass retained by a solid phase, χ_s, is given by

$$\chi_s = \frac{C_s\, m_s}{C_w\, V + C_s\, m_s} \tag{3}$$

Here, V is the total volume of the aqueous phase, and m_s is the mass of sorbent

present. Dividing through by $C_w V$ allows Eq. 3 to be rewritten in terms of K_d and the solids concentration, S

$$\chi_s = \frac{K_d\, S}{1 + K_d\, S} \tag{4}$$

Thus, the overall movement of a solute is a function of both the distribution coefficient and substrate concentration. Equation 4 can be used to demonstrate the environmental significance of K_d. Consider the effluents passing through the primary clarifier. The solids level in these effluents will be low (typically around 500 mg/L),[28] and solutes will have concentrations between 1 ppb and 1 ppm.[29] If the solids-water K_d value for a compound is 30 mL/g (a conservative example), the calculated total solute retention by the solids is less than 2%, indicating that sorption by primary clarifier solids is not a significant removal mechanism. But for a compound with an aqueous effluent concentration of 100 ppb, the sludge concentrations will be about 3 ppm (i.e, a 30-fold increase over the solute's effluent concentration prior to secondary treatment). Thus, the solids have a substantial solute concentration despite their ineffectiveness in removing the solute load from effluent streams. In fact, whenever a solute's K_d value is greater than 1, its concentration will be magnified in the solid phase. In this project, the goal is to develop a method for predicting this level of magnification. With increasing pressures to reduce landfill and incineration loads, this will help the assessment of potential risks connected with alternative disposal practices for primary sludge.

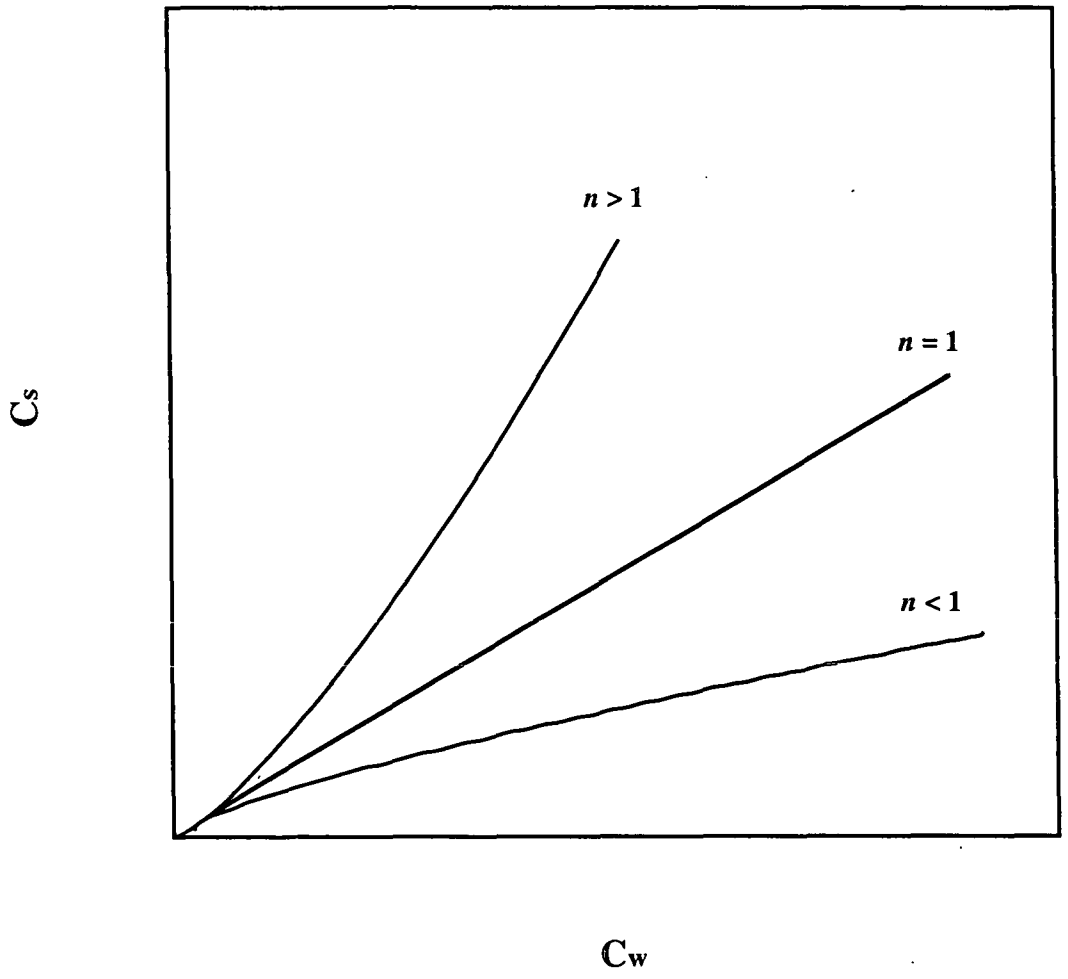


Figure 1. Three types of observed Freundlich isotherms for the sorption of organics to natural solids.

The Additive Nature of K_d

The sorption of solutes by a solid phase is additive; that is, it can be broken down into contributions from its various components or phases. In terms of a distribution coefficient this can be stated as

$$K_d = f_1 K_1 + f_2 K_2 + \cdots + f_n K_n = \sum_{i=1}^{n} f_i K_i \quad (5)$$

where the f terms are the mass fractions of a material in the sorbent and the K terms are the solid-water distribution coefficients for the individual phases. Splitting K_d like this is useful for modeling purposes when the different phases have significantly different sorption behavior. For example, soil and sediment material is composed of an aggregate of organic and mineral particles. Highly decomposed plant and animal material consisting of proteins, lignin, cellulose, and an array of other decomposition products make up the organic fraction, while materials such as sand, silt, and clay compose the mineral fraction. Applying Eq. 5, K_d for the aqueous sorption of organic solutes to these natural sorbents can split as

$$K_d = f_{om} K_{om} + f_{min} K_{min} \quad (6)$$

where f_{om}, f_{min}, K_{om}, and K_{min} are the mass fraction and solid-water distribution coefficients for the organic and mineral phases, respectively. Measurements of K_d values for soils and sediments at variable organic contents indicate that although the organic fraction typically composes $< 5\%$ of the mass, it appears to dominate the sorption.[20,30–32] This allows Eq. 6 to be rewritten as

$$K_d \approx f_{om} K_{om} \tag{7}$$

This indicates that sorption of an organic solute by soils and sediments can be determined from the mass fraction of organic material present and the organic-water distribution coefficient. Thus, by taking advantage of the additive nature of sorption in this system, the development of predictive relations was considerably simplified. A similar approach for pulp fibers is outlined in Chapter 3.

Thermodynamics of Sorption

An approach which has been successful in modeling the distribution of nonpolar or weakly polar organic solutes between an aqueous solution and a soils and sediments treats the process as a phase distribution.[19,33,34] In an aqueous solution, it is argued that the mineral-bound hydrophobic organic material in a soil or sediment exists primarily as polymer chains coiled into globular units, similar in structure to aqueous globular proteins[35–40] or micelles.[41–46] These units are believed to have a nonpolar interior into which organic solutes can partition to escape to the aqueous phase. On the basis of this model, the solid-water distribution of a solute can be treated as a phase distribution between a nonpolar solvent and water. From a thermodynamic standpoint, this is stated as

$$\mathcal{F}_{om} = \mathcal{F}_w \tag{8}$$

where $\mathcal{F}_{om}$ and $\mathcal{F}_w$ are the fugacities of a solute in the organic and water phase,

respectively. Rewriting fugacities in terms of activity coefficients and mole fractions leads to

$$x_{om}\ \gamma_{om} \;=\; x_w\ \gamma_w \tag{9}$$

which can be rearranged to

$$K_p \;=\; \frac{x_{om}}{x_w} \;=\; \frac{\gamma_w}{\gamma_{om}} \tag{10}$$

where K_p is the partition coefficient. This can be converted into the form of a distribution coefficient using the molar volume and density of the organic phase, $\overline{V}_{om}$ and ρ_{om}, respectively, and the molar volume of the water phase, $\overline{V}_w$

$$K_{om} \;=\; \frac{x_{om}\ \overline{V}_w}{x_w\ \overline{V}_{om}\ \rho_{om}} \;=\; \frac{\gamma_w}{\gamma_{om}}\ \frac{\overline{V}_w}{\overline{V}_{om}\ \rho_{om}} \tag{11}$$

The relation between K_d and the last form of Eq. 11 is the basis for most predictive relations, and in Chapter 3 implicit use of it will be made in the development of a linear free-energy relationship (discussed below). In Chapter 4, Eq. 11 will be more explicitly used in the development of equations predicting the effects of temperature and inorganic salts. This type of extension of the partitioning model has been suggested, but there is little data to prove that it works.

Linear Free-Energy Relationships (LFERs)

LFERs are used in a number of disciplines for the prediction of rate and equilibrium constants.[47–52] In this section, the development of a LFER between an organic solute's soil or sediment organic-water distribution coefficient, K_{om}, and its octanol-water distribution coefficient, K_{ow}, is described. As discussed above, the sorption of organic solutes by soils and sediments is often modeled as a phase transfer which results in Eq. 11 or in log form as

$$\log\ K_{om} \ = \ \log\ \gamma_w \ - \ \log\ \gamma_{om} \ + \ \log\ \frac{\overline{V}_w}{\overline{V}_{om}\ \rho_{om}} \tag{12}$$

The activity coefficient of a solute is related to its partial molar excess free energy in a phase as

$$\left(\frac{\partial g^E}{\partial n}\right)_{T,P} \ = \ RT\ ln\ \gamma \tag{13}$$

This allows Eq. 12 to be rewritten as

$$\log\ K_{om} \ = \ \frac{-\triangle G^E_{om}}{2.303RT} \ + \ \log\ \frac{\overline{V}_w}{\overline{V}_{om}\ \rho_{om}} \tag{14}$$

where $\triangle G^E_{om}$ is the molar excess free energy change associated with a solute's transfer from an aqueous solution into the organic phase. Defining the free energy of transfer, $\triangle G_{om}$, as

$$\triangle G_{om} \;=\; \triangle G^{E}_{om} \;-\; 2.303RT \log \frac{\overline{V}_w}{\overline{V}_{om}\;\rho_{om}} \tag{15}$$

allows $\log K_{om}$ to be written in terms of $\triangle G_{om}$ as

$$\log\; K_{om} \;=\; \frac{-\triangle G_{om}}{2.303RT} \tag{16}$$

Variations in the free energy of transfer can be expressed at constant temperature by

$$d\triangle G_{om} \;=\; \Big(\frac{\partial \triangle G_{om}}{\partial x}\Big)_T\, dx \;+\; \Big(\frac{\partial \triangle G_{om}}{\partial y}\Big)_T\, dy \;+\; \cdots \tag{17}$$

For a finite change in x from some arbitrary standard value x_0 to x_i while the other variables are held constant, the free energy change will be given by

$$\triangle G^{i}_{om} \;-\; \triangle G^{0}_{om} \;=\; \Big(\frac{\partial \triangle G_{om}}{\partial x}\Big)_T\,(x_i \;-\; x_0) \;=\; g^{x}_{om}\,(x_i \;-\; x_0) \tag{18}$$

The variable x can represent various independent variables. For example, x may represent the number of chlorine atoms on a phenolic compound or the molecular weight of a family of organic compounds. In these situations, the g^{x}_{om} term would then represent the increase or decrease in the free energy of transfer per addition of a chlorine atom or increase in molecular weight, respectively. A similar development can be followed for the distribution of an organic solute between octanol and water which produces

$$\log\ K_{ow}\ =\ \frac{-\triangle G_{ow}}{2.303RT} \tag{19}$$

$$\triangle G^{i}_{ow}\ -\ \triangle G^{0}_{ow}\ =\ (\frac{\partial \triangle G_{ow}}{\partial x})_{T}\ (x_i\ -\ x_0)\ =\ g^{x}_{ow}\ (x_i\ -\ x_0) \tag{20}$$

Here, K_{ow} is the solute's octanol-water distribution coefficient. Arbitrarily defining this transfer of the initial (x_0) solute as the reference state (i.e., $\triangle G^{0}_{ow} = 0$), we have

$$(x_i\ -\ x_0)\ =\ \frac{\triangle G^{i}_{ow}}{g^{x}_{ow}} \tag{21}$$

Substituting equation Eq. 21 into Eq. 18 gives

$$\triangle G^{i}_{om}\ =\ \frac{g^{x}_{om}}{g^{x}_{ow}}\ \triangle G^{i}_{ow}\ +\ \triangle G^{0}_{om} \tag{22}$$

and, finally, rewriting this in terms of distribution coefficients produces

$$\log\ K_{om}\ =\ a\ \log\ K_{ow}\ +\ b \tag{23}$$

where

$$a\ =\ \frac{g^{x}_{om}}{g^{x}_{ow}} \tag{24}$$

and

$$b = \Delta G^0_{om} \tag{25}$$

Parameters a and b may be obtained through linear correlations of Eq. 23. A successful correlation of data depends strongly on the behavior of a. For a to remain constant, the free energy change for both the solid-water and octanol-water transfer associated with the variable x (i.e., g^x_{om} and g^x_{ow} in Eq. 24) must remain constant or change in a parallel fashion. For nonpolar and moderately polar organic compounds at low concentrations, the activity coefficients in both aqueous phases are approximately the same and will be similarly small (i.e., close to 1) in both the octanol and organic solid phases. Because g^x_{om} and g^x_{ow} are related to the change in excess free energy of a phase transfer, this results in an a value of close to 1. An example of this would be correlations for aromatic hydrocarbons in which x represents a moderate increase in molecular weight or molecular surface area. Even correlations with more polar compounds are possible when the dominant transfer mechanism is the same for all compounds, resulting in g^x_{om} and g^x_{ow} values that change in the same proportion for each solute (i.e., $a \neq 1$, but constant). Correlations typically become poorer when compounds of various polarities and functionalities, especially those capable of forming hydrogen bonds, are studied, which may result in significantly different activity coefficients in the octanol and organic solid phases. This is the reason that LFERs developed within a chemical family are usually more accurate than those which cross family lines.

THESIS OBJECTIVES

The objective of this thesis research was to develop a greater understanding of the dominant interactions responsible for the distribution of an organic chemical at low concentrations between an aqueous solution and wood pulp-derived solids. The ultimate goal was the development of predictive equations which could be adapted for use under various conditions. Such equations would provide a means to better understand the transport of organic chemicals during wastewater treatment or engineer the adhesion of organic materials to fibrous substrates.

A METHOD FOR THE LIQUID SCINTILLATION COUNTING OF SORBED ^{14}C-LABELED CHLOROPHENOLS AND EXPERIMENTAL PROCEDURES

INTRODUCTION

The distribution behavior of an organic chemical is most effectively studied through the use of ^{14}C-labeled radioisotopes, which enables quantitative measurements to be made at extremely low concentrations.[53] For compounds that have a strong affinity to the solid phase, experimental measurements of K_d are easily made from changes of ^{14}C activity in the solution phase. But, for compounds that sorb less strongly, the measurements of distribution coefficients are complicated by the need to make a direct measurement of the activity retained by the sorbent. This is the case for the sorption of ^{14}C-labeled chlorophenols to pulped wood fibers.[54] In addition to chemical quenching caused by contaminants in the scintillation cocktail, the liquid scintillation counting (LSC) of isotopes sorbed to the fibers is interfered with by color quenching and self-absorption. Color quenching is caused by residual amounts of the darkly colored lignin material which optically blocks the photons generated in the scintillation mechanism. Self-absorption is a restriction to the release of radioactive particles by the sorbent and may occur whenever an isotope is adsorbed to a nonscintillating material. The level of chemical and color quenching can be quantified with a Horrocks or H number which is a general measure of the amount of quenching occurring in a liquid scintillation sample and allows for various correction techniques to be applied.[53] On the other hand, there is no measure of the amount of self-absorption which occurs in a system; thus, when counting solid-retained isotopes, desorption is crucial to accurate counting. Figure 2 demonstrates the effect of increasing lignin levels on

the counting efficiency of [^{14}C] 2,4,5-trichlorophenol. In this case, the radioactivity was added after the scintillant to isolate quenching effects (i.e., no self-absorption) by avoiding isotope sorption. Both curves extrapolate to the same initial efficiency level at zero mass, but, while the fibers with their color completely bleached out have no effect on the scintillation counting, increasing the amount of fibers containing lignin (kappa number 69.8) dramatically reduces counting efficiencies (Eq. 26). This heavy color quenching combined with potential self-absorption losses makes it impossible to accurately measure sorbed ^{14}C activity by simply counting the fibers.

Conventional means for eliminating error caused by color quench and self-absorption involve the dissolution and decolorization of the adsorbent,[53,55] but the combined presence of lignin and cellulose makes wood materials difficult to dissolve without strong thermal and chemical treatment. This can result in large isotope losses, especially in the case of volatile organics such as chlorophenols. The first half of this chapter examines the difficult task of measuring fiber-sorbed isotope concentrations. A comparison is made of three simple recovery techniques for quantifying the sorption of ^{14}C-labeled organics to wood fibers without the need for extensive processing. The first involves the wet ashing of fibers and the sampling of $^{14}CO_2$ from an alkaline trap.[56] This is the most complicated of the three approaches because it involves the chemical treatment of the fibers outside the scintillation vial. In the other two techniques, the fibers are treated directly in the scintillation vials prior to counting. In one approach, the color of the fibers is removed using domestic bleach, and the compounds are presumed to be desorbed from the solid phase by the addition of scintillation cocktail.[57] For the other, the fibers are leached using methanol and distilled water to desorb the isotope, and efficiency corrections are made from quench curves produced from dried fibers.

Recovery experiments proved this final technique to be the more accurate approach, and, in the next section of this chapter, its use in the measurement of fiber-water distribution coefficients, K_d, as well as other experimental methods used in this project will be described.

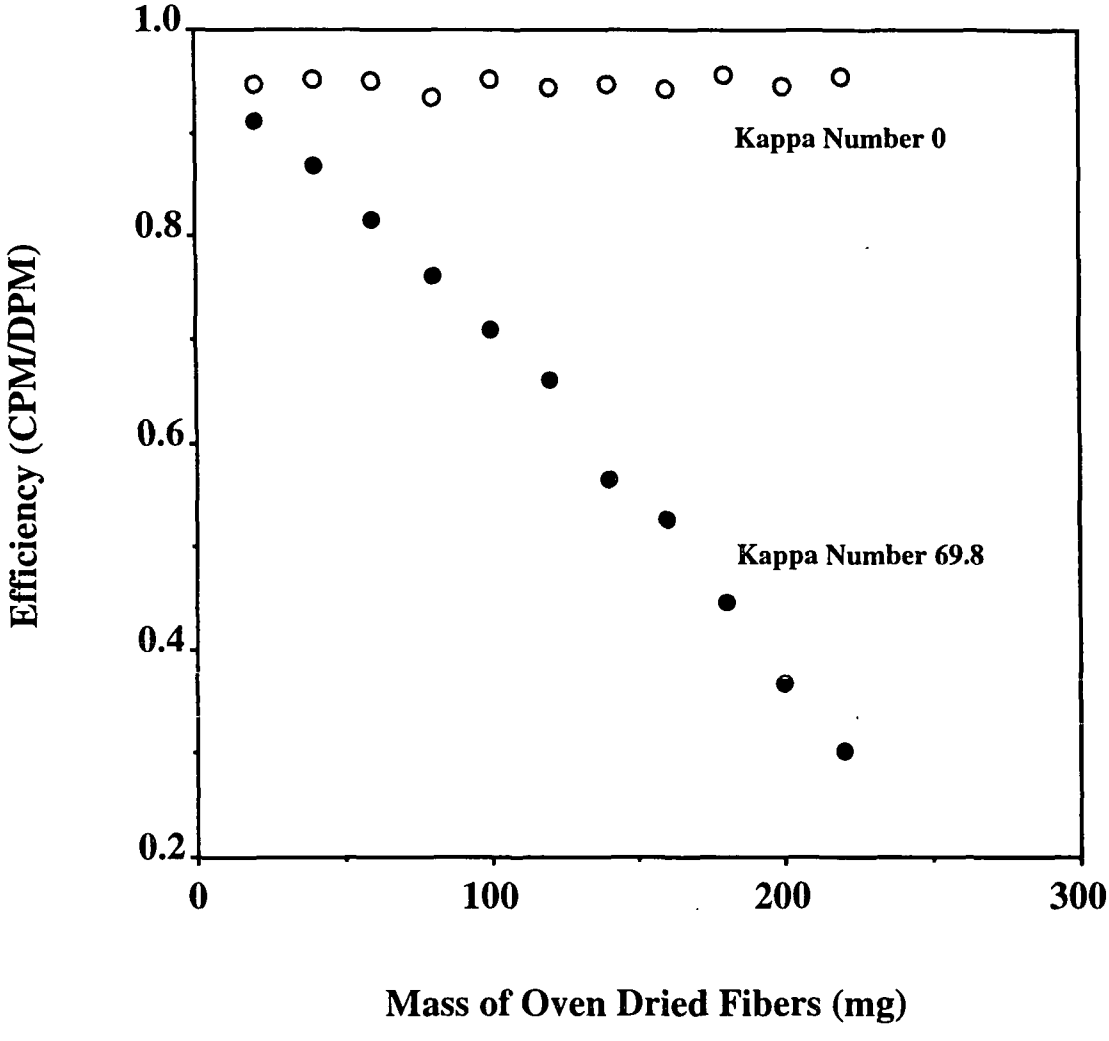


Figure 2. The effects of fiber mass on the liquid scintillation counting efficiency of [^{14}C] 2,4,5-trichlorophenol for fibers at two lignin levels.

MATERIALS

Softwood pulp fibers and cotton linters (100% cellulose fibers) were obtained from Georgia-Pacific Corporation. The pulp fibers were thoroughly washed to remove residual processing chemicals, and the average kappa number (lignin content) of each sample was determined.[58] The fibers were centrifuged to a 30% consistency (solids content) and stored at 5°C. The consistency of the samples was never allowed to rise above 35% to preserve the pore structure of the fibers. Model lignin material, which is precipitated from the effluents of softwood pulping operations and sold under the commercial name Indulin® AT, was obtained from the Westvaco Chemical Division (Charleston Heights, SC) as dry powder. Nonlabeled organic compounds (cold analytes) used as solutes and cosolutes in sorption studies (> 98% pure) were purchased from either Chemservices (West Chester, PA) or Absolute Standards (Hamden, CT). Radiolabeled chemicals were purchased from Sigma Chemical Company (St. Louis, MO). Both [^{14}C] 2,4-dichlorophenol (8.42 mCi/mmol) and [^{14}C] 2,4,5-trichlorophenol (4.40 mCi/mmol) were stored in amber vials as methanol solutions at 2°C. 2,4-Dichlorophenol was > 98% pure, and 2,4,5-trichlorophenol was > 99% pure as determined by HPLC. Scintillation counting was done on a Beckman (Fullerton, CA) Model LS 3801 Scintillation Counter. Scintiverse™ E Scintillation Cocktail (Fisher, Pittsburgh, PA) was used for all solution phase samples. Sigma-Fluor™ Universal LSC Cocktail was used with the fiber samples.

RECOVERY EXPERIMENTS

Methods

For the adsorption reactions in the wet ashing and substrate decolorization procedure, 10 mL of pH 7 buffered distilled water were combined with 100 mg (oven-dried) kappa number 23.9 pulp fibers in amber vials with Teflon®-lined caps. 2,4-Dichlorophenol (103 nCi) was added through a methanol carrier, and the components were thoroughly mixed and allowed to equilibrate. It was found that four days were more than sufficient for equilibration (see kinetics section). The fibers were then separated from the aqueous phase using vacuum filtration and placed either in a 12-mL sealable glass vial for wet ashing or directly into a 20-mL scintillation vial for decolorization. For mass balance determinations, triplicate measurements were made of the separated solution phase at a window setting of 300-670, and efficiency corrections were carried out with chemical quench curves generated using ^{14}C standards purchased from Beckman.

The wet ashing procedure was based on a method described by Spiller and Stallings.[56] Initially, the fibers were decomposed with 3 mL of concentrated H_2SO_4 which produced a dark brown solution. A 30% H_2O_2 solution (300 μL) was then added, and the mixture was gently hand mixed to further facilitate oxidation. After about 10 minutes, the resulting yellow solution was heated clear on a hotplate at 85°C for 10 minutes. The entire procedure was carried out in a sealed vial containing a 1.5-mL conical microcentrifuge tube filled with 500 μL of 2 M NaOH solution. The NaOH solution acted as a trap for the $^{14}CO_2$ released from chlorophenol compounds which were oxidized along with fibers. After the mixture cooled, volume adjustments were

done on the trap solution, and 100 μL aliquots were counted to determine the total activity contained in the fibers. Counting was done at a window setting of 300-670, and corrections were made with the generated chemical quench efficiency curves.

The substrate decolorization technique was a modified version of the method described by Smith and Lang.[57] Here, the fibers were placed directly into a loosely capped 20-mL glass scintillation vial and decolorized using 3 mL of a 25% (v/v) domestic bleach solution (equivalent to 1.25% sodium hypochlorite) at 55°C for two hours. The decolorized sample was then treated with 45 μL of 4 M NH_4OH solution to remove the strong chemiluminescence caused by the unreacted hypochlorite. After a lag of 30 minutes to allow the nitrogen bubbles from the reaction between the ammonia and hypochlorite to dissipate, 100 μL of acetic acid and 17 mL of scintillation cocktail were added, and the samples were incubated for 12 hours. Counting was done at a window setting of 400-670 to avoid the high level chemiluminescence associated with the bleached samples. Quench corrections were performed using chemical quench efficiency curves generated for this window setting.

For the solvent extraction procedure, the adsorption experiment was run directly in a 20-mL scintillation vial to allow for a recovery determination without the need for a separation of the water and fiber phases. Water (4.32 mL) was combined with 50 mg of pulp fibers and either 28.8 nCi of [^{14}C] 2,4-dichlorophenol or 9.21 nCi [^{14}C] 2,4,5-trichlorophenol. The vials were mixed and placed in the dark to prevent photooxidation of the chlorophenol structures. After four days, 4.32 mL of methanol and 180 μL of glacial acetic acid (to reduce chemiluminescence) were added, the vials were mixed and incubated for 15 minutes, and 12 mL of scintillant was then added. H number was determined daily, and it was found that five days of clarification was

sufficient for the samples to reach an equilibrium H number (i.e., a minimum). The samples were then counted with a window setting of 0-670. Color quench curves were generated by adding various amounts of pulp fibers ranging from 40 to 60 mg. With the quenching from the brown color of the fibers being the only factor of concern in the generation of the quench curves, the fibers could be dried to much higher consistencies allowing for significantly more accurate mass measurements.

Results and Discussion

The reason for testing three recovery techniques was the failure of the first two to provide an accurate method for measuring isotope distributions. Initially, the wet ashing procedure appeared to be the most promising approach because it avoided liquid scintillation counting of the sorbent. But the recoveries of [^{14}C] 2,4-dichlorophenol from the fibers based on a mass balance were highly variable and frequently fell below 50%. The decolorization of fibers was successful in eliminating color quenching, but the thermal treatment and nitrogen released from the ammonia reaction with residual hypochlorite appeared to strip the compound out of solution. This resulted in [^{14}C] 2,4-dichlorophenol solid phase recoveries of $< 70\%$. Since these techniques failed to eliminate the interference caused by the fibers in counting the sorbed isotopes, the remaining alternative was to correct for these interferences with external standards.

The use of color quench curves (Fig. 3) generated from dried fiber in combination with the methanol/water extraction approach proved to be superior in accounting for the sorbed chlorophenols. Table 2 lists the overall recoveries for both [^{14}C] 2,4-dichlorophenol and [^{14}C] 2,4,5-trichlorophenol for three different fiber samples. Each value is an average of seven measurements. All recoveries were $> 98\%$, and most were

> 99% with excellent reproducibility (< ±1.5%). The use of overall recoveries can be deceptive if sorption is small, but for these samples, conditions were used which would ensure strong sorption. The mechanism assumed in this approach is the generation of identical chemical quenching for each sample, and the nearly complete desorption of isotopes from the fiber.

Table 2. Percent recoveries of ^{14}C-labeled chlorophenols from pulped wood fibers using methanol-water extraction and quench correction functions.

kappa number	recovery percentage	
	2,4-dichlorophenol	2,4,5-trichlorophenol
23.9	98.4	99.4
83.7	99.2	99.1
105	98.7	100

Chemical quenching variations were kept to a minimum by repeating the identical procedure including the use of the same equipment and brand of supplies for all samples. This allows the use of a single correction for the combined chemical and color quenching losses. The physical nature of the bond typically involved in the sorption of neutral organics to purely organic substrates[59,60] should allow for the complete desorption of the retained organics with the correct solvent combination. The choice of methanol and water for leaching the fiber samples was based on the need both to disperse the fibers (water) and to modify the hydrophobic forces (methanol). This combination produced an excellent dispersion of the fibers even after 12 mL of the scintillation cocktail were added, allowing for an even settling of the fibers to produce highly reproducible equilibrium H number measurements.

Although the extraction procedure was highly successful in recovering sorbed isotopes, there were major difficulties in applying it to sorption measurements. Mass levels of the samples had to be limited to 50 mg to optimize the accuracy of the quench corrections. Since pulped wood fibers are composed mainly of cellulose, they tend to retain moisture which adds considerable uncertainty to fiber weight. In order to maintain the pore structure of the fibers for the sorption experiments, the 50-mg fiber samples were weighed at a consistency of about 35% (65% moisture). This resulted in mass errors of as much as 20%, and more than 20% error in the measured distribution coefficients. Thus, the benefits of a highly accurate recovery technique did not translate into accurate distribution coefficients. Fortunately, the even settling of fibers in the scintillation vials produced an H-number measurement which was highly sensitive to mass variations. By plotting the quench data as oven-dried fiber mass vs. H number, lines for predicting mass levels could be generated (mass determination curve). Figure 4 is a mass determination curve for the kappa number 69.8 fibers. The curve is simply a plot of the data used in Fig. 3, but, instead of efficiency, the oven-dried mass that produced the quenching is plotted. The application of the solvent extraction approach in combination with quench and mass correction functions is demonstrated in Fig. 5 for the sorption isotherm of ^{14}C-labeled 2,4,5-trichlorophenol by pulped wood fibers. The plot shows the data from the initial fit in which the mass for the solid phase concentration measures was based on attempts accurately to weigh 50 mg of fiber (on oven-dried basis). It also shows the significantly better fit produced from data in which the mass determination function is used for the same calculation.

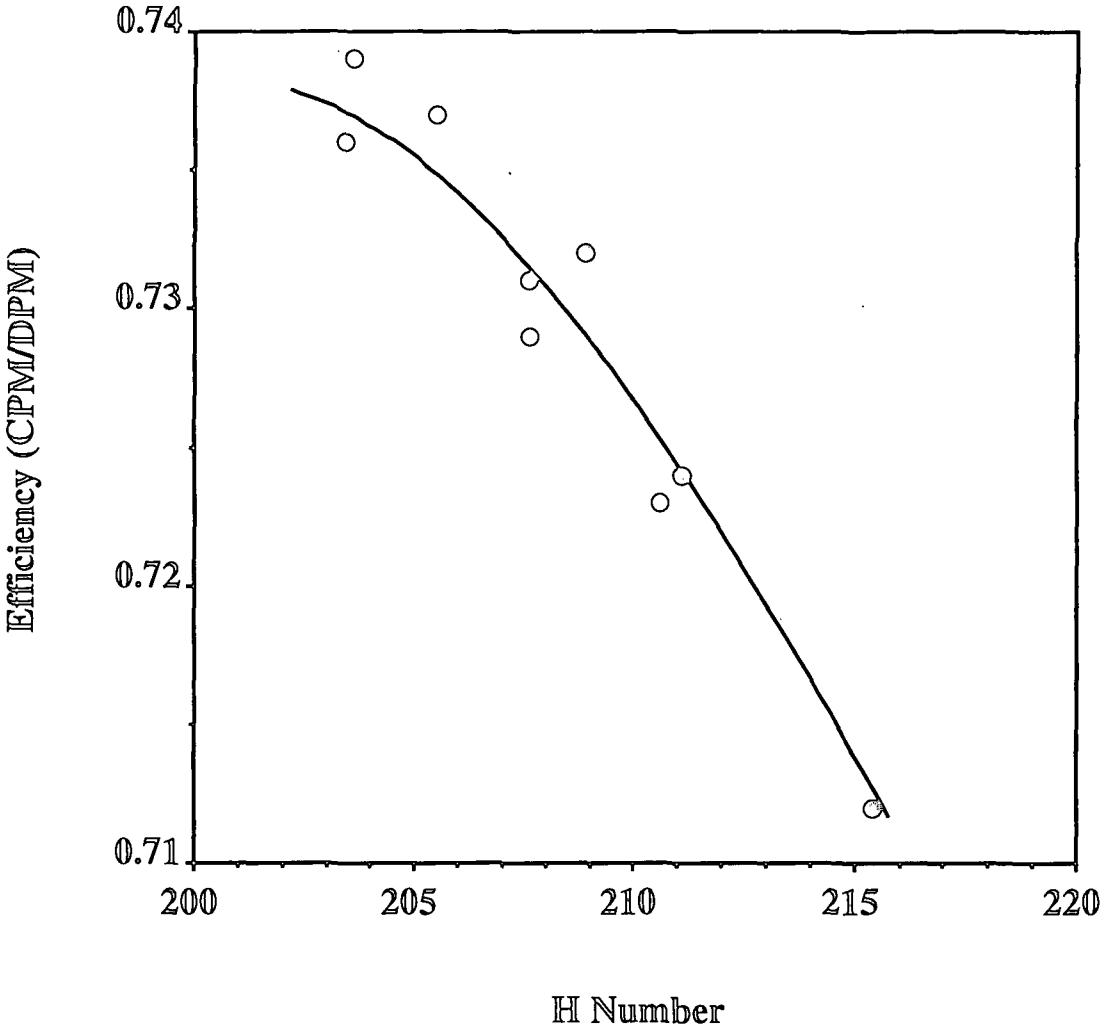


Figure 3. ^{14}C quench curve for kappa number 69.8 softwood fibers.

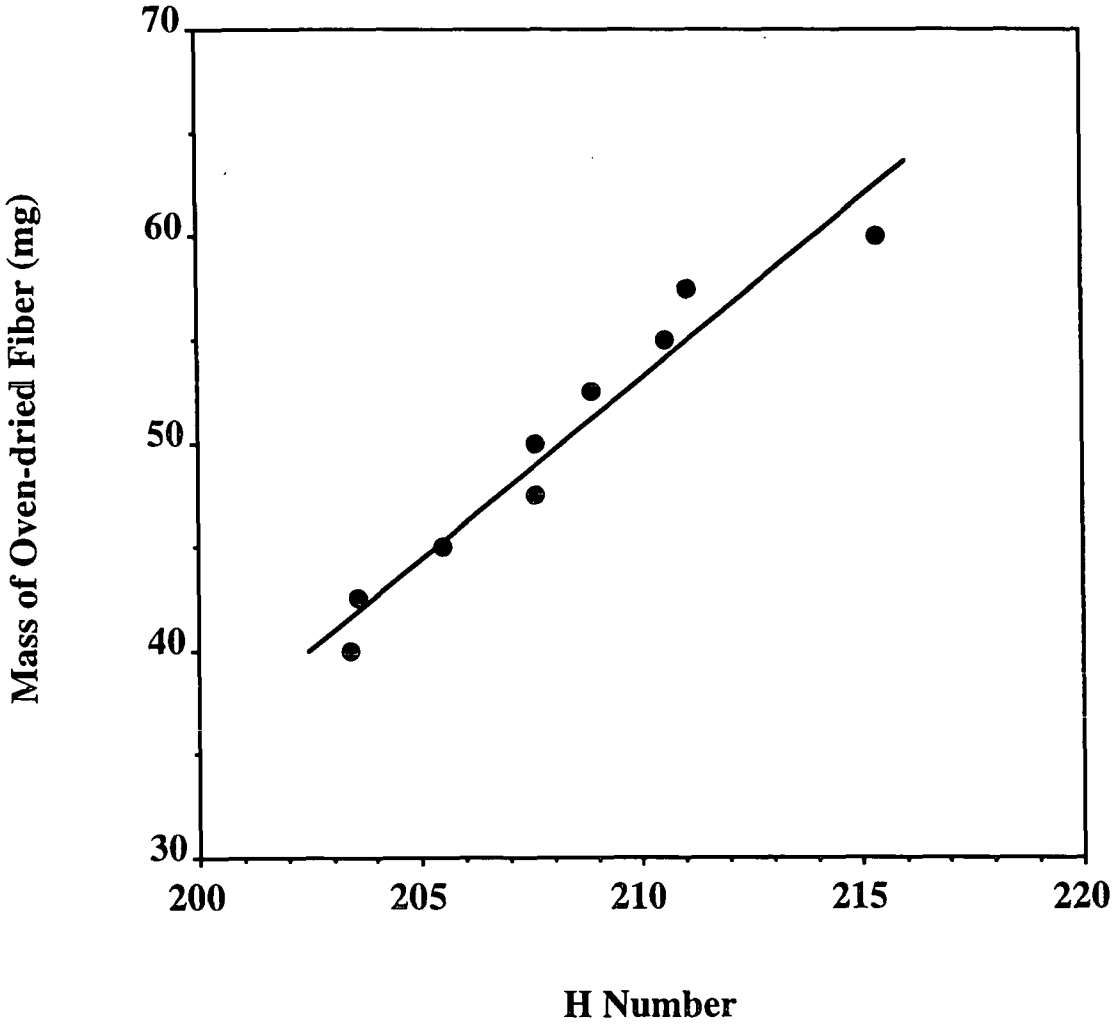


Figure 4. Mass curve for kappa number 69.8 softwood fibers.

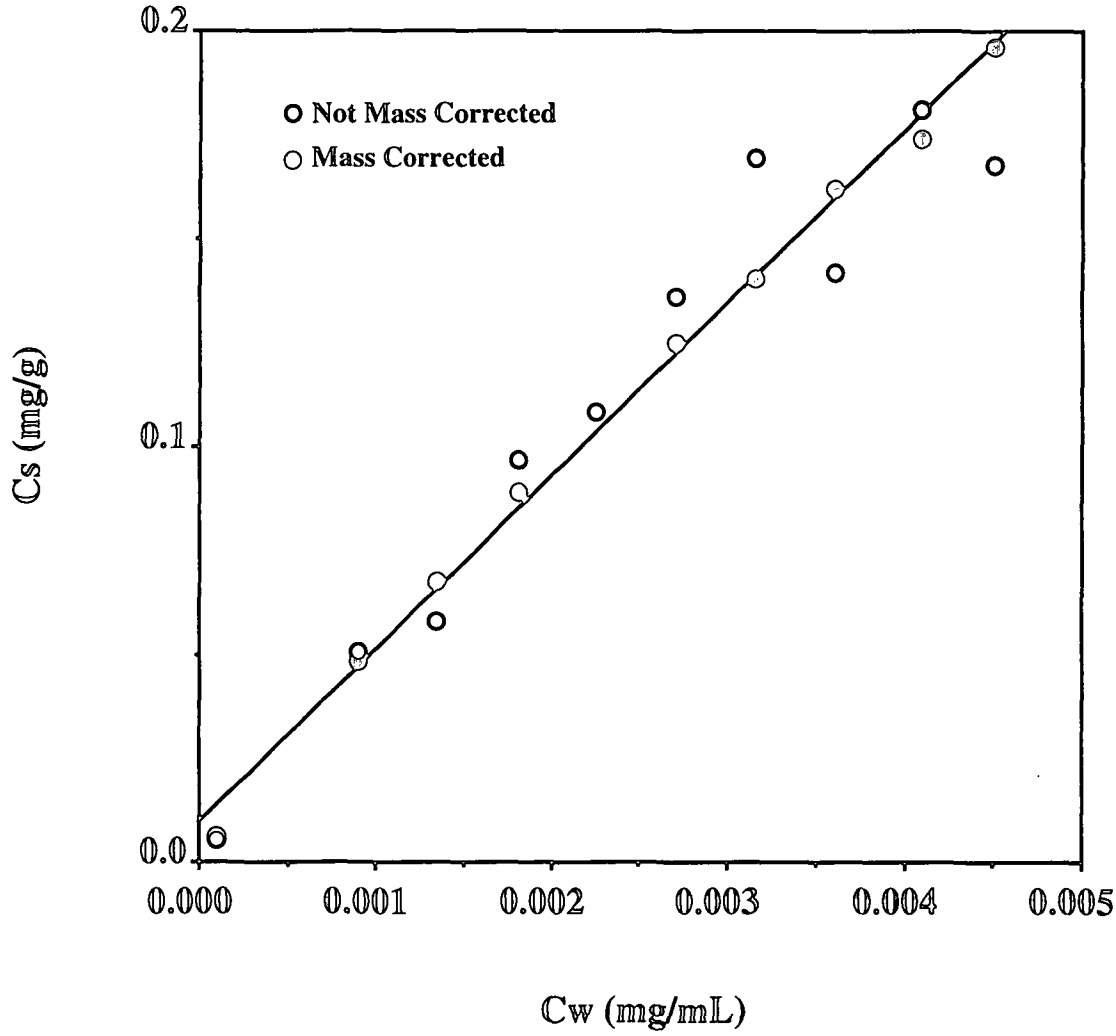


Figure 5. Sorption isotherm linear fits with ($C_s = 0.0098 + 41.6C_w, r^2 = 0.995$) and without ($C_s = 0.0152 + 39.3C_w, r^2 = 0.924$) the use of the mass determination technique for the retention of 2,4,5-trichlorophenol to kappa number 69.8 softwood fibers.

EXPERIMENTAL METHODS

Measurements of K_d

The success of the methanol-leaching and mass-determination approach led to its being used in the measurements of K_d values throughout this project. Figures 6-14 include some of the efficiency and mass curves for the softwood pulp samples used in the project. The fiber curves were generated by the procedure described in the previous section using standards containing a fiber mass of between 40 and 60 mg (oven-dried). Mainly as a matter of convenience, the isotope being studied was used in the generation of quench curves (e.g., in 2,4,5-TCP sorption studies, [^{14}C] 2,4,5-TCP was used to generate curves). As is standard practice for color and chemical quench curves, third-order polynomials were used to fit the data, while the mass data appeared to be best fit with linear correlations. The constants of these fits were determined through a least-squares fit of the data. The figures demonstrate a strong correlation for most samples (Table 3), but this did tend to decrease with decreasing kappa number. For kappa numbers 4.93 and 0 (cotton linters), the poor correlation of the efficiency curves led to the use of an average efficiency correction. For kappa number 0 fibers, the correlation between mass and H number was also poor, but, in the case of kappa number 4.93 fibers, the correlation remained strong and was used. A periodic check was made for the accuracy of the efficiency and mass determinations, and occasionally it became necessary to produce new curves.

Sorption experiments were run by adding about 50 mg (oven-dried based on consistency measurements) to 18 mL of distilled water in 20-mL precleaned amber vials with Teflon®-lined caps. The slurry was mixed on a vortex mixer until the fibers be-

came completely dispersed, and the samples were allowed to stand for more than eight hours. Stock solutions of either [^{14}C] 2,4-dichlorophenol or [^{14}C] 2,4,5-trichlorophenol were produced by adding the solute (through a methanol carrier) to distilled water in an amber volumetric flask (500 mL). A magnetic stir bar was added, and the stock solution was stirred for eight or more hours. Solute concentration was checked through the scintillation counting of multiple aliquots (250 μL). Once it was confirmed the solute was in solution, 3 mL was transferred to sorption samples to produce final aqueous phase volumes of 21 mL. Samples were then sealed, and their components were thoroughly mixed and allowed to equilibrate (four days, see kinetics section). Concentrations of the 2,4-DCP or 2,4,5-TCP in samples varied depending on the experiment but were generally at 100 ppb. The aqueous phase used in experiments was either distilled water adjusted for pH using small amounts of HCl and NaOH or an aqueous buffer. For measurements on the effect of inorganic salts, either buffers adjusted for ionic strength with KCl or KCl solutions adjusted for pH with small amounts of HCl and NaOH were used. When inorganic salt effects were not being studied, ionic strength levels of the aqueous phase were kept below 0.005 M. It should also be noted that for measurements in which fiber concentrations were varied, 50 mg (oven-dried) of fiber was used and the volume of water was varied.

Table 3. Polynomial fits of efficiency or quench curves and linear fits of mass curves.

kappa number	function	r^2
105	$E = -15.994 + 0.21152(H\#) - 8.5229 \times 10^{-4}(H\#)^2$	0.968
	$+1.0717 \times 10^{-6}(H\#)^3$	
	$m_f = -315.63 + 1.7004(H\#)$	0.945
83.7	$E = 140.13 - 2.0051(H\#) + 9.6456 \times 10^{-3}(H\#)^2$	0.922
	$-1.5512 \times 10^{-5}(H\#)^3$	
	$m_f = -343.43 + 1.8441(H\#)$	0.937
69.8	$E = -92.628 + 1.3262(H\#) - 6.2676 \times 10^{-3}(H\#)^2$	0.960
	$+9.8536 \times 10^{-6}(H\#)^3$	
	$m_f = -309.52 + 1.7269(H\#)$	0.944
32.3	$E = -23.656 + 0.3349(H\#) - 1.5206 \times 10^{-3}(H\#)^2$	0.851
	$+2.2829 \times 10^{-6}(H\#)^3$	
	$m_f = -280.14 + 1.5717(H\#)$	0.851
23.9	$E = 127.73 - 1.9083(H\#) + 9.6020 \times 10^{-3}(H\#)^2$	0.897
	$-1.6102 \times 10^{-5}(H\#)^3$	
	$m_f = -380.64 + 2.0844(H\#)$	0.903
4.93	$E_{ave} = 0.8883 \pm 0.0060$	
	$m_f = -196.03 + 1.3074(H\#)$	0.832
0	$E_{ave} = 0.9109 \pm 0.0037$	

After equilibration, the fibers were separated from the aqueous phase using vacuum filtration. The filters used were 0.02 μm, 47 mm anodized aluminum (Alltech, Deerfield, IL). Trials demonstrated that the retention of solutes by these membranes was negligible, and their use in filtration process had no impact on the measurement of the distribution coefficients. The filters had the added benefit of being reusable after a cleaning with ethanol. After separation, the fibers were lifted from the filter and placed in a 20-mL scintillation vial containing methanol (4.32 mL), distilled water (4.32 mL), and glacial acetic acid (180 μL). The contents of the vials were briefly mixed on a vortex mixer to disperse the fibers. Triplicate aliquots (250 μL) taken from the filtrate were placed in scintillation vials (20 mL), 15 mL of scintillation cocktail was added, the contents were mixed on a vortex mixer, and the samples were placed in counting racks. After a number of solid samples were collected (usually about 12), 12 mL of scintillation cocktail was added, the contents were mixed, and the solid samples were also placed in counting racks. The filtrate samples were counted immediately following the experiments, but solid samples were not. As described in the recovery experiments, it was necessary to allow the fibers to settle out of the scintillation cocktail to produce a constant H number (about five days).

Filtrate and fiber samples were counted without automatic quench compensation[53] at window settings of 300-670 and 0-670, respectively. For all samples, a 20-minute count was used, and an average H number was determined using 10 measurements. For filtrate samples, CPM (counts per minute) measurements were converted to DPM (disintegrations per minute) using counting efficiency values, E, calculated from chemical quench curves (Fig. 15)

$$DPM = \frac{CPM}{E} \tag{26}$$

DPM values for the solid phase samples were determined in a similar fashion using the efficiency curves for a specific kappa number. The mass in the samples was determined by using the measured H number and mass curves (see Figs. 6-14). From these measurements, the fiber-water distribution coefficient, K_d, for a sorption sample is determined as

$$K_d = \frac{\frac{DPM_f}{m_f}}{\frac{DPM_s}{V_s}} \tag{27}$$

where m_f and V_s are the mass of fiber (oven-dried) used in sorption experiment and the volume of solution sampled from filtrate, respectively, and DPM_f and DPM_s are the fiber and solution phase activities measured, respectively. With fiber mass units in mg and filtrate volume units in μL, the resulting distribution coefficient has units of μL/mg or mL/g.

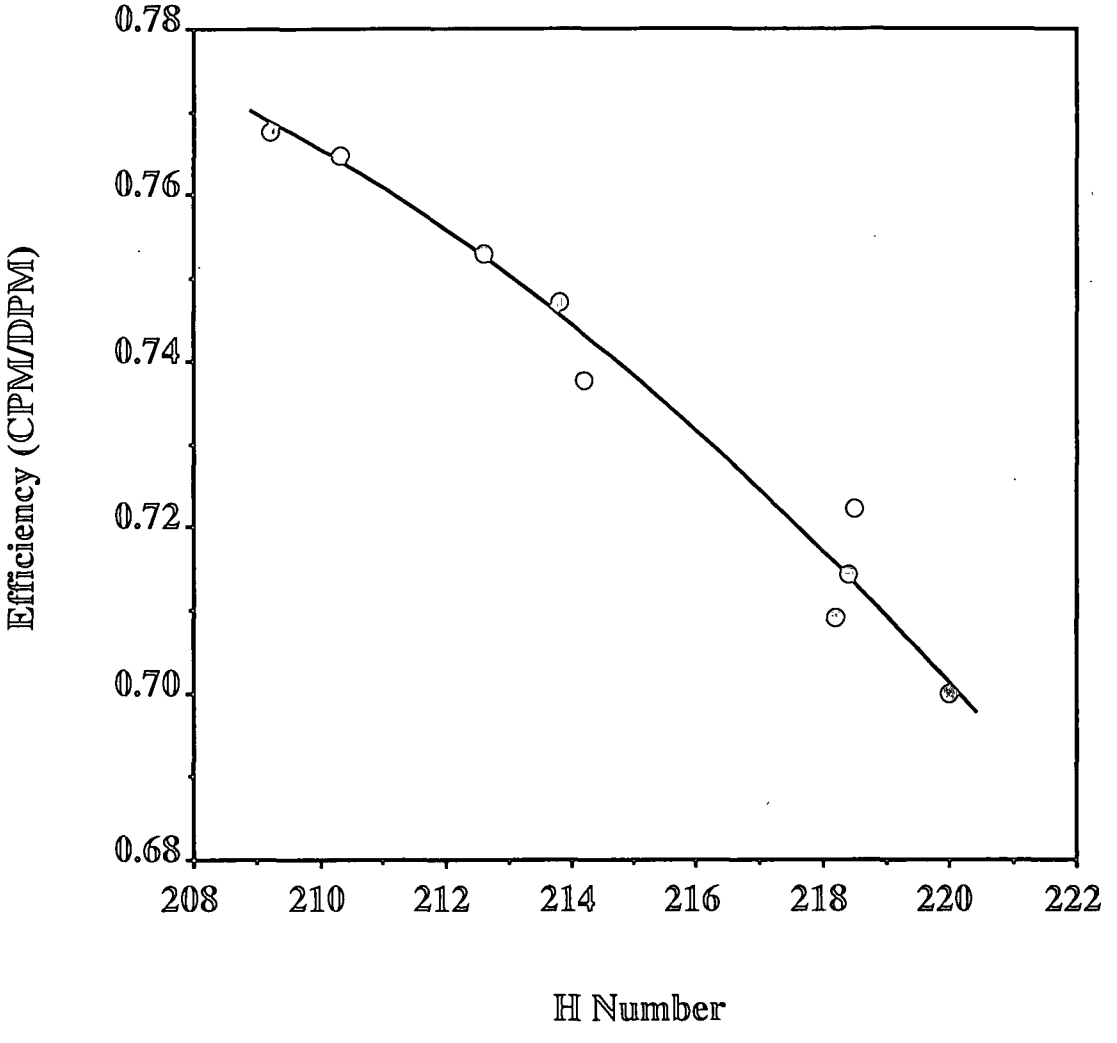


Figure 6. ^{14}C quench curve for kappa number 105 softwood fibers.

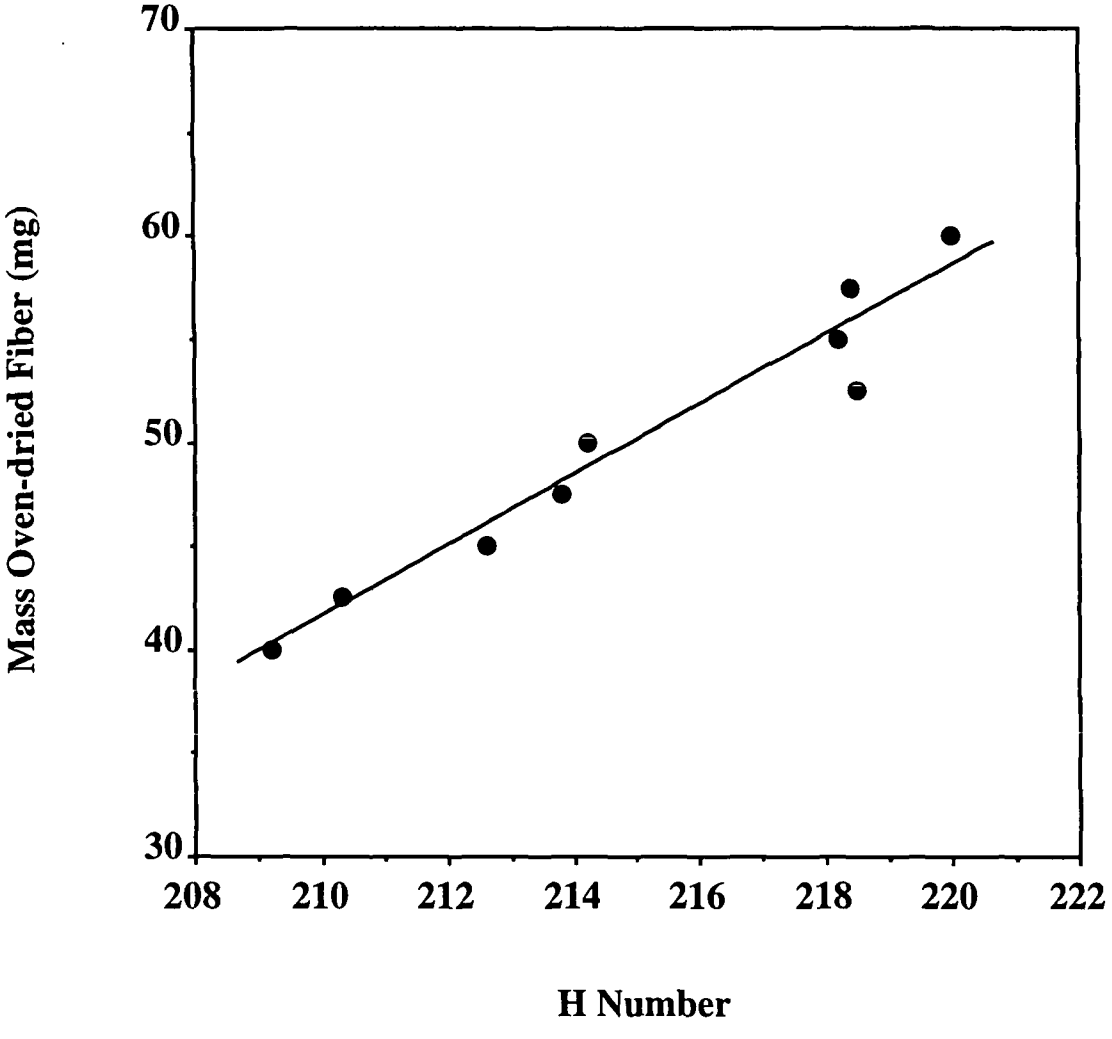


Figure 7. Mass curve for kappa number 105 softwood fibers.

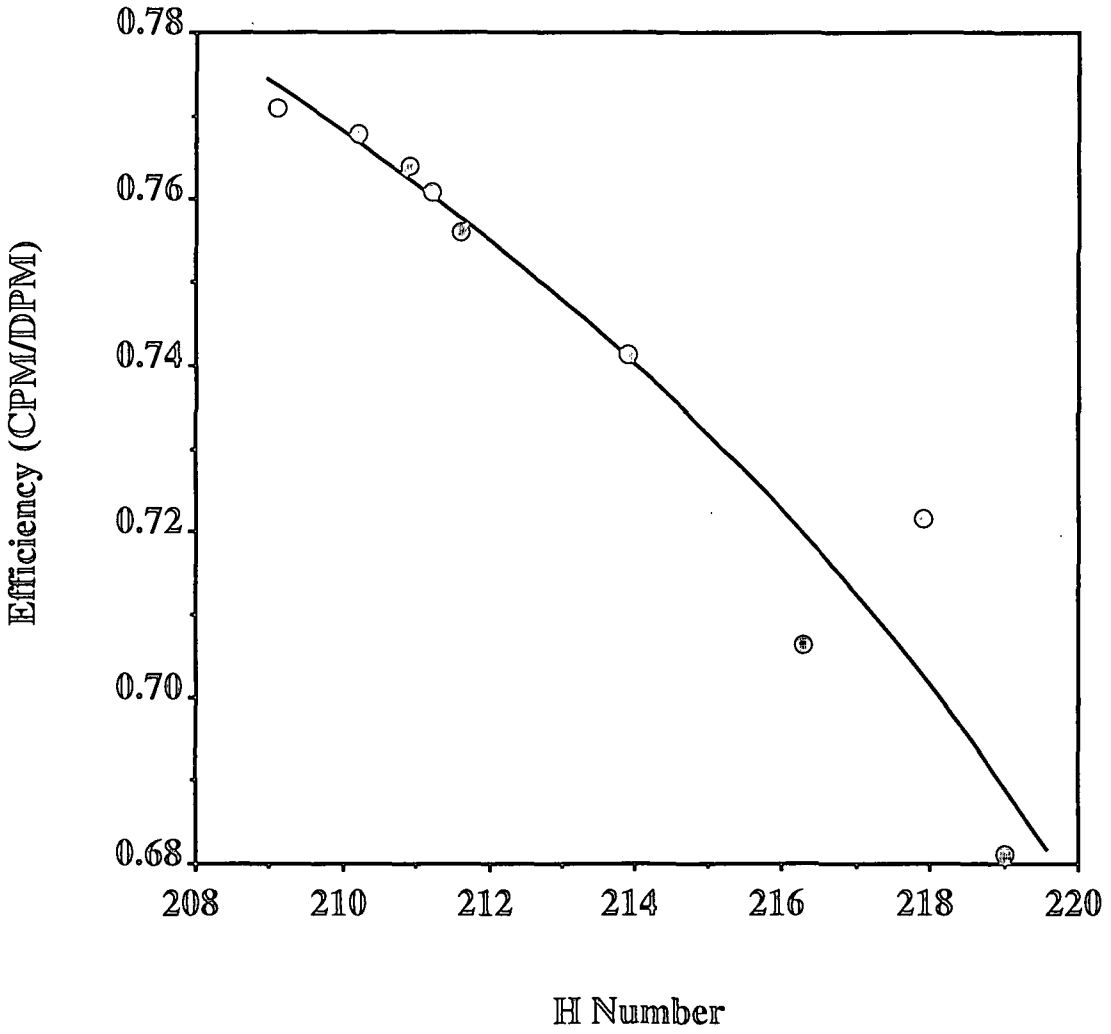


Figure 8. ^{14}C quench curve for kappa number 83.7 softwood fibers.

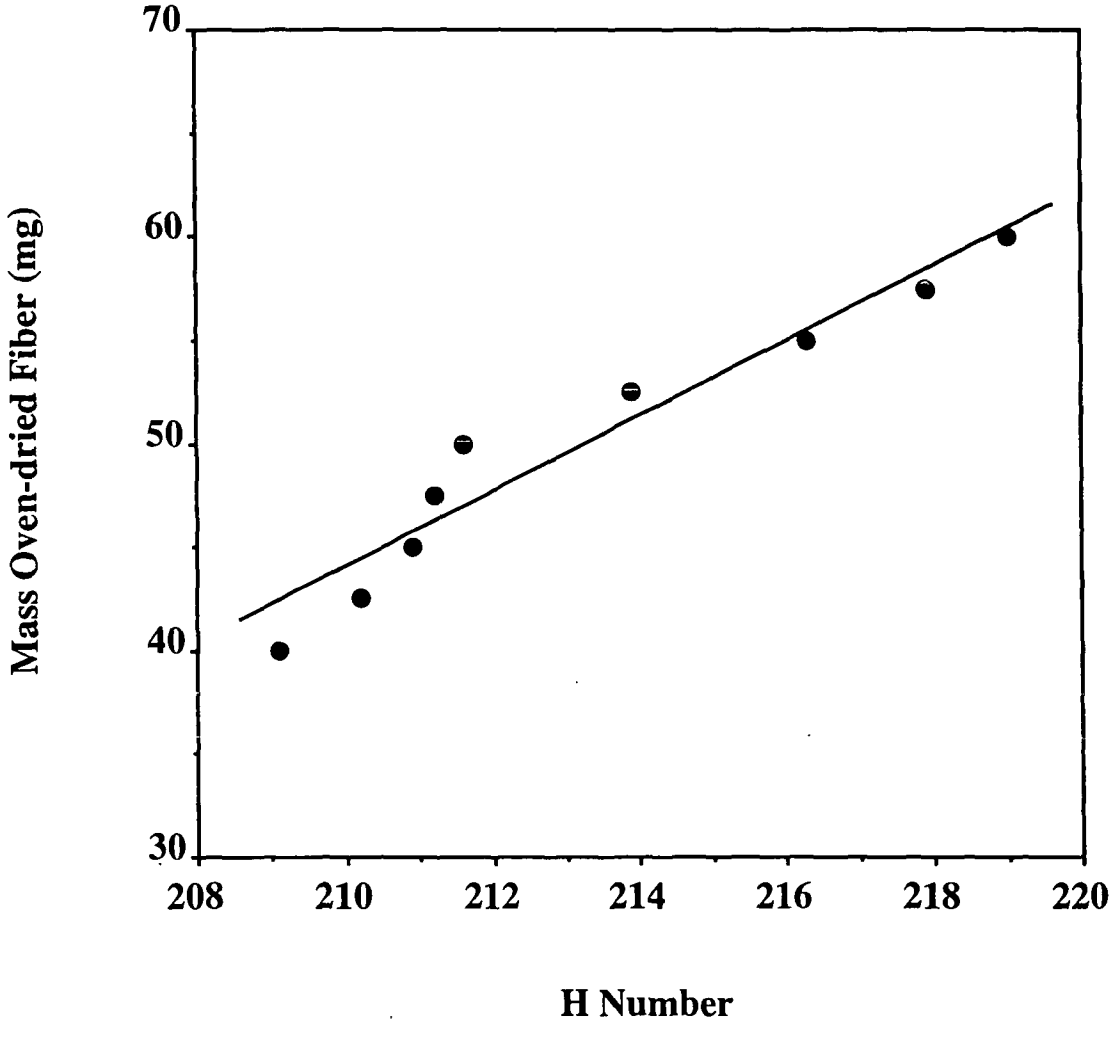


Figure 9. Mass curve for kappa number 83.7 softwood fibers.

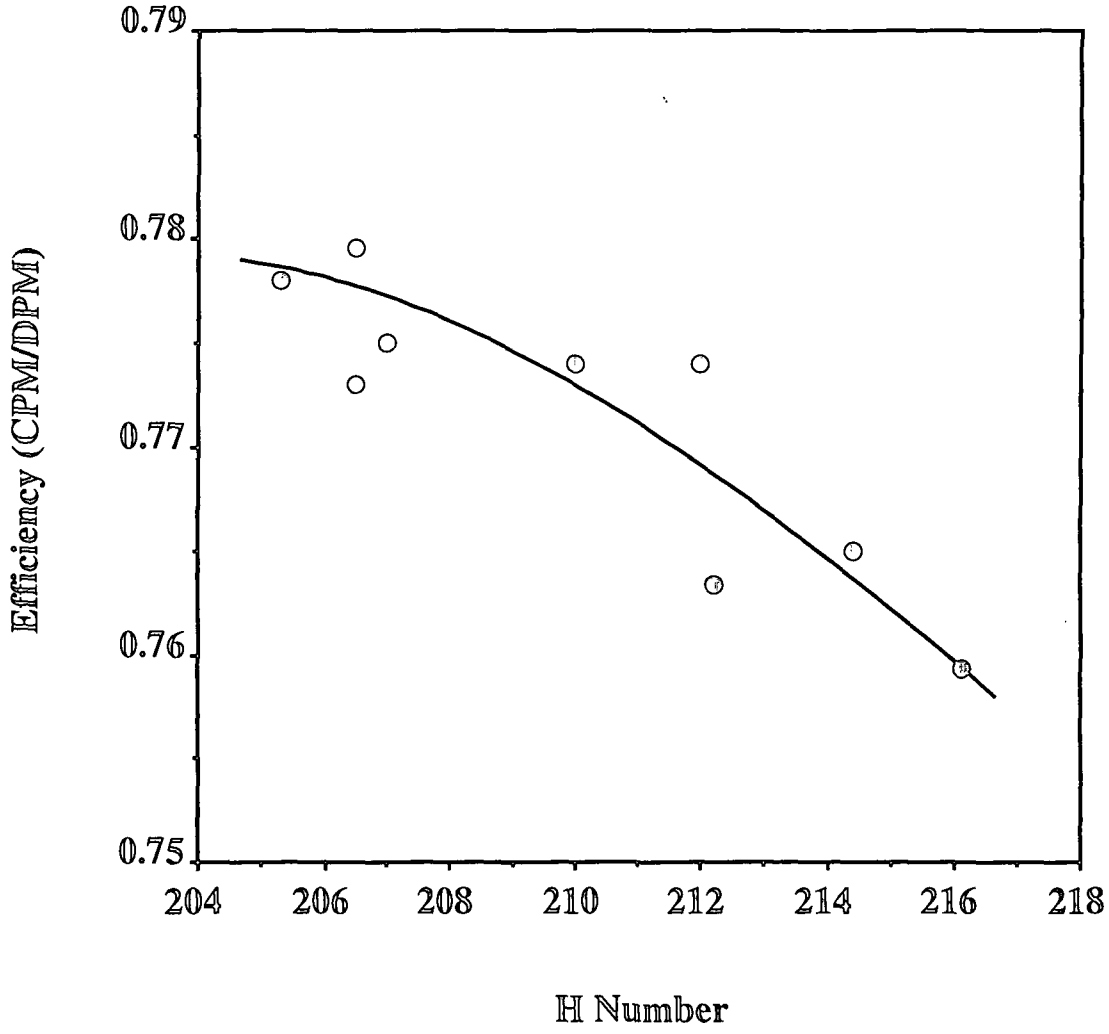


Figure 10. ^{14}C quench curve for kappa number 32.3 softwood fibers.

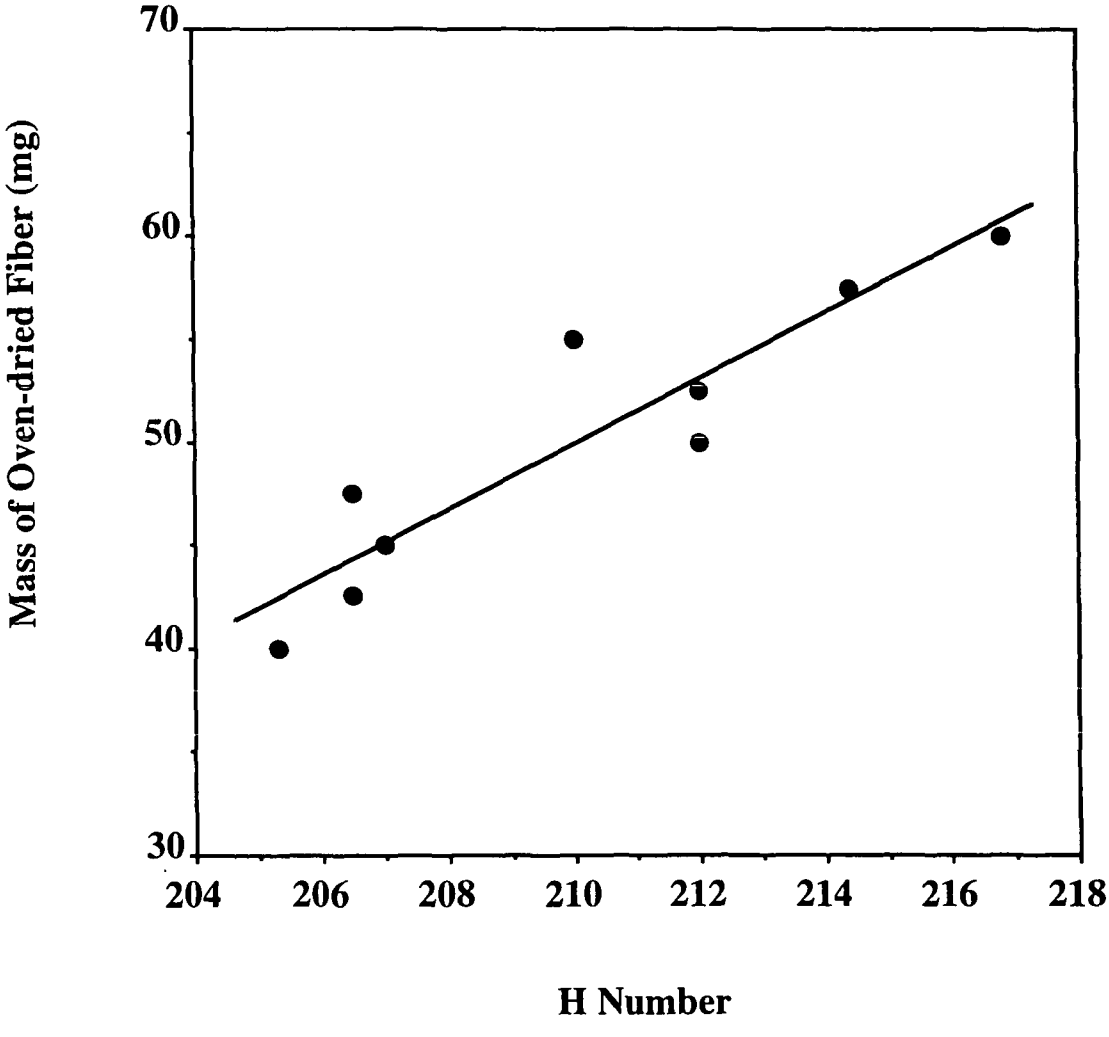


Figure 11. Mass curve for kappa number 32.3 softwood fibers.

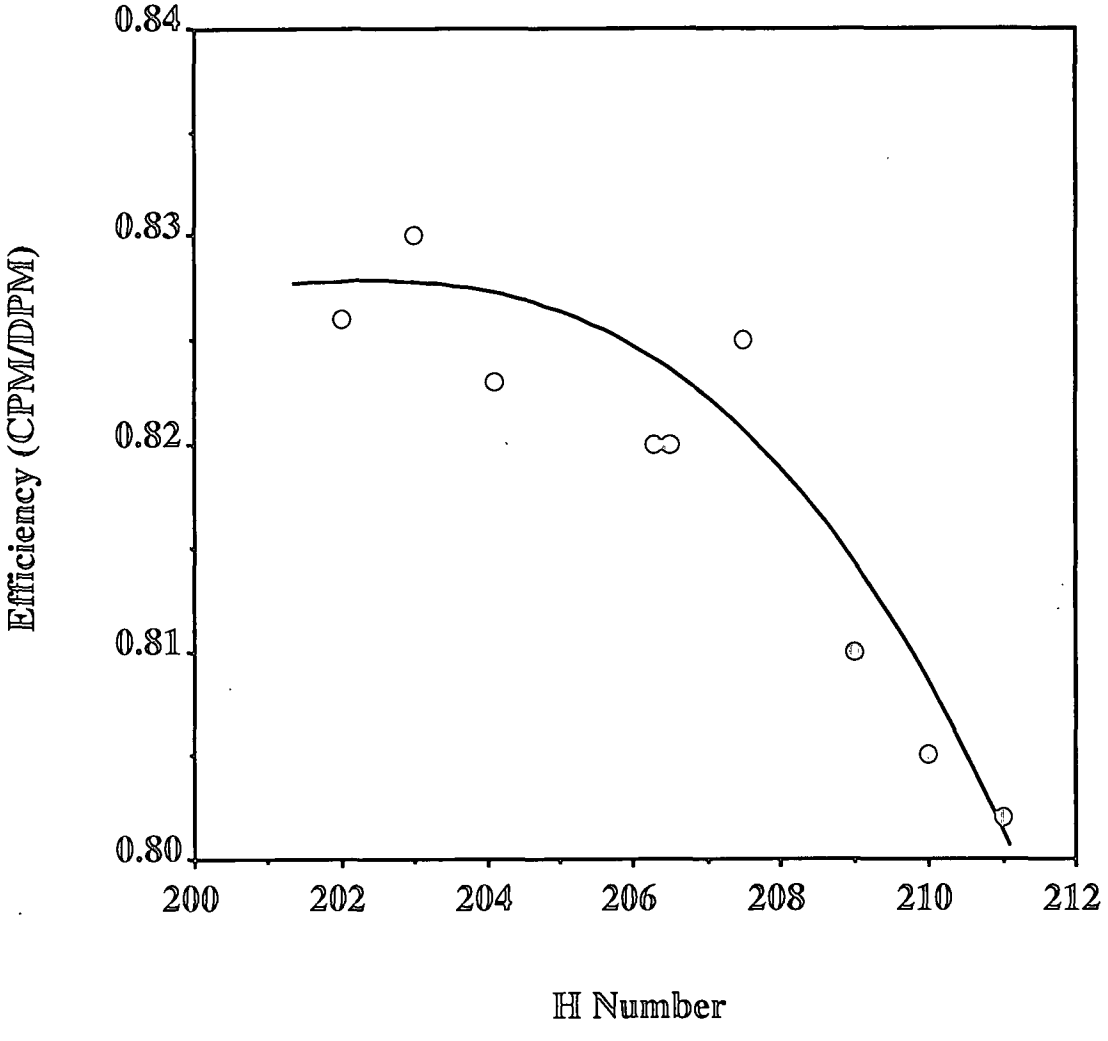


Figure 12. ^{14}C quench curve for kappa number 23.9 softwood fibers.

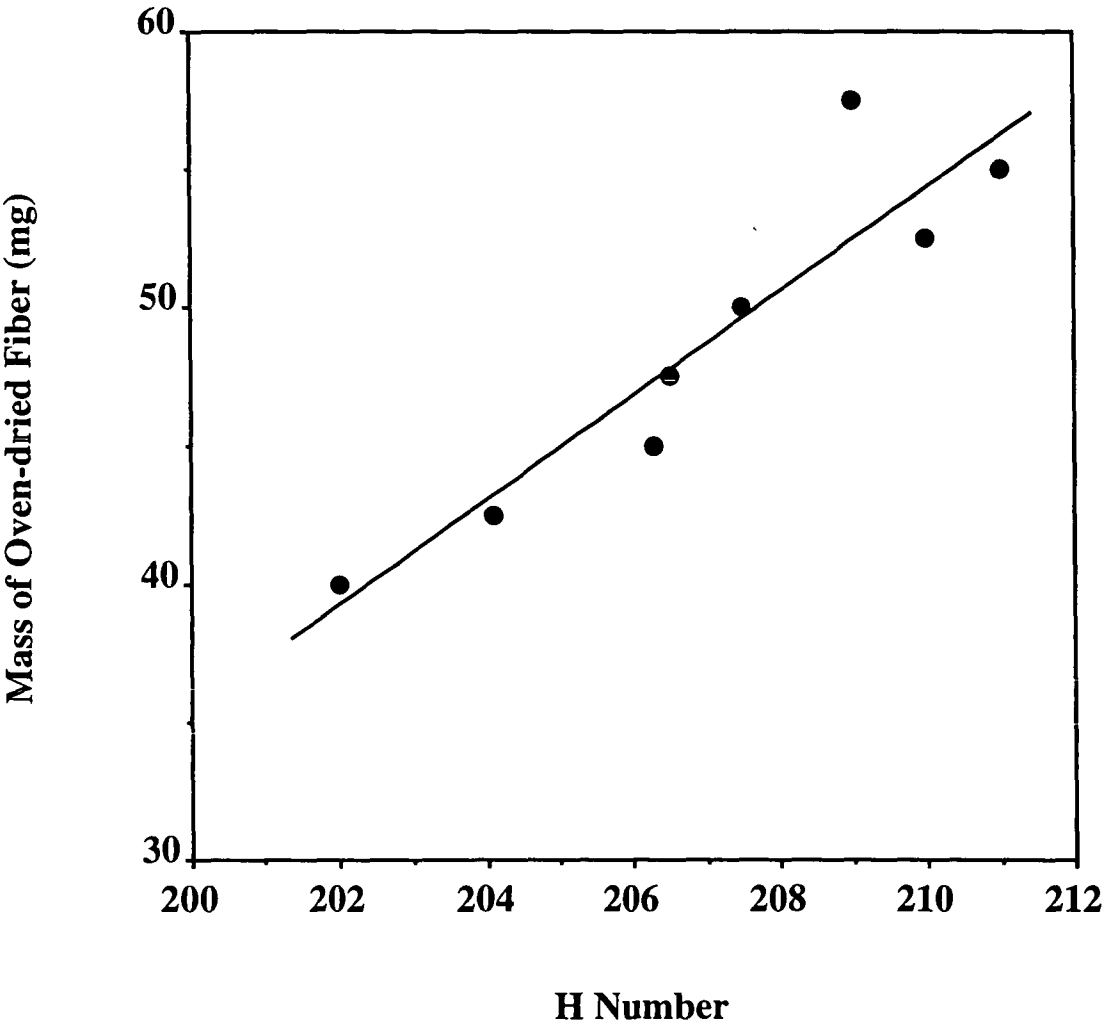


Figure 13. Mass curve for kappa number 23.9 softwood fibers.

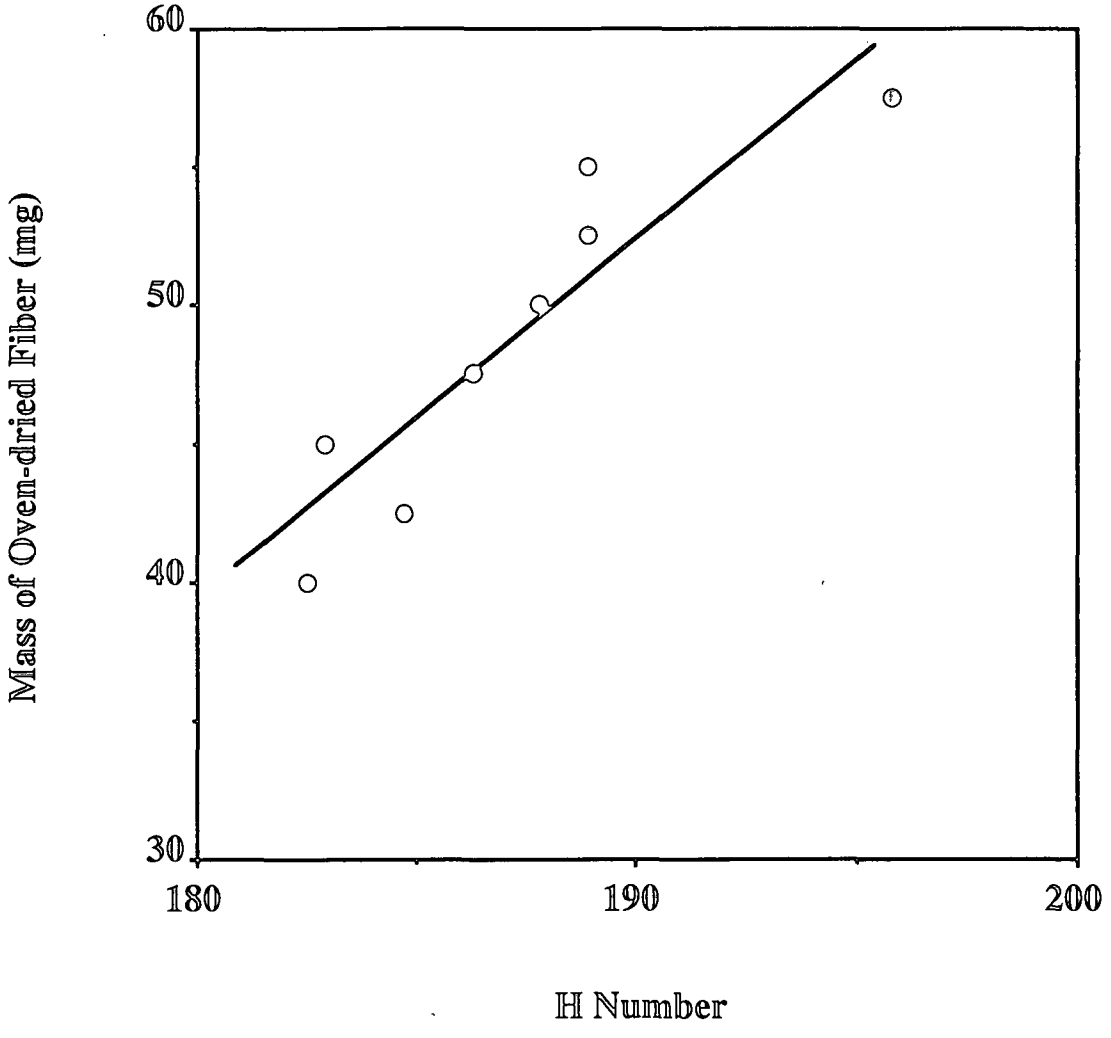


Figure 14. Mass curve for kappa number 4.93 softwood fibers.

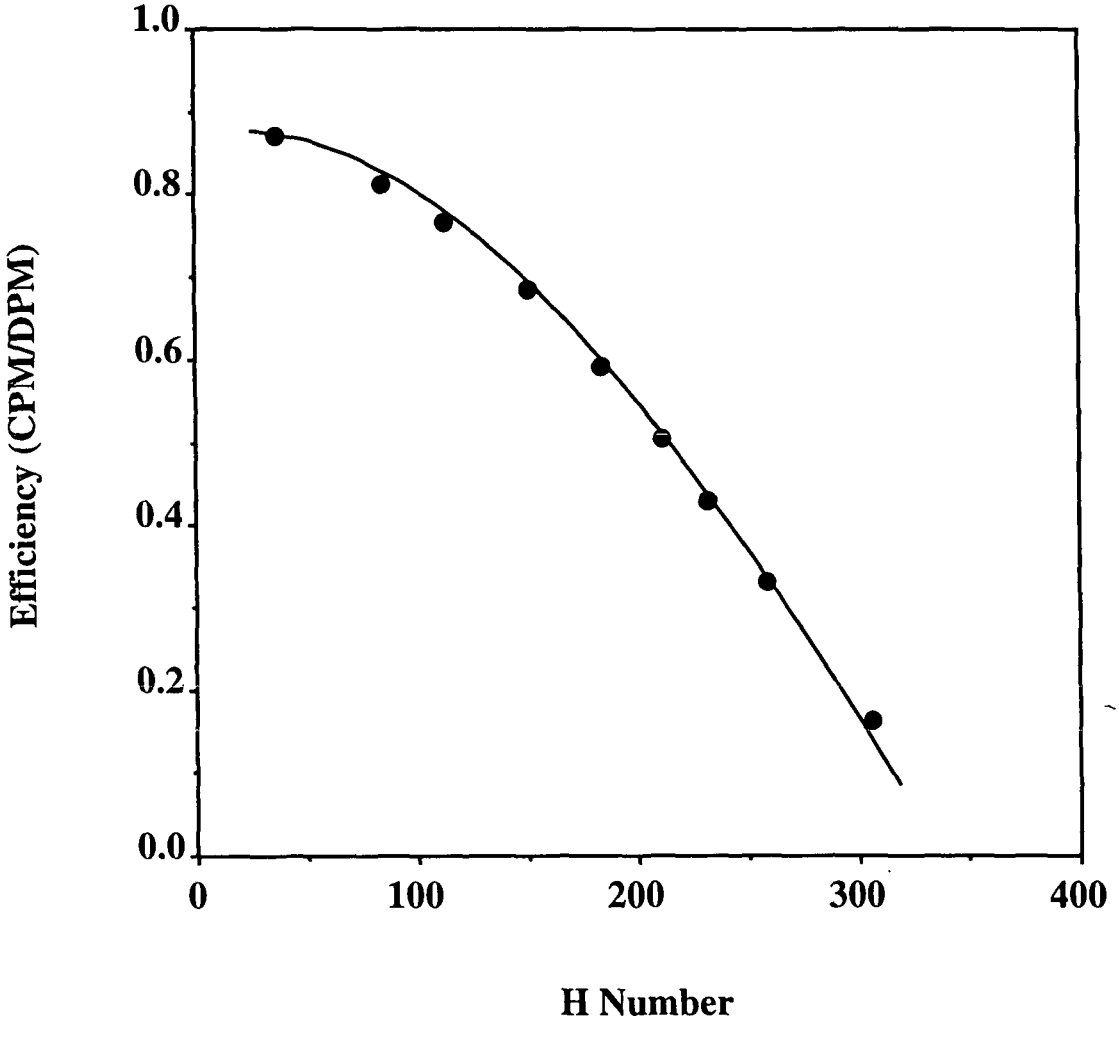


Figure 15. Chemical quench curve for a window setting of 300-670.

Determination of Acid Dissociation Constants

Differences in the reported ionization constants found for 2,4-DCP and 2,4,5-TCP from various sources made it necessary to measure these pK_a values under the same pH, temperature, and low ionic strength conditions used in the sorption studies. Since the conjugate bases of both the di- and trichlorophenol had significantly different absorption spectra from those for their acid form, ionization constants could be determined through absorption spectroscopy and pH measurements (i.e., "mixed acidity constants"). The details of this approach are described elsewhere.[61] Spectra were taken on a Perkin-Elmer (Norwalk, CT) Model Lambda 4B UV/VIS Spectrophotometer. The results of the pK_a determinations at 25°C were 7.87 ± 0.05 for 2,4-DCP and 6.92 ± 0.02 for 2,4,5-TCP in distilled water adjusted for pH using weak HCl and NaOH solutions. Inorganic salt effects on pK_a values of both 2,4-DCP and 2,4,5-TCP were measured for use in interpreting sorption data at various pH levels. Values measured at 1 M KCl showed little change from pK_a values measured when no salt was present ($< 1.5\%$ drop).

Measurements of Fiber Consistency and Solution Retention

Consistency values of fiber samples, C_f, defined as the ratio between oven-dried and wet fiber mass, were determined using a Mettler (Hightstown, NJ) model PC 180 heated (110°C) analytical balance. The amount of solute retained by the water in fibers in sorption experiments, k_w, was estimated by measuring the consistency of fibers separated from water using vacuum filtration. The wet fibers were produced by following the same procedure as that used in sorption experiments, equilibrating 21 mL of an aqueous buffer and 50 mg of fiber in 20-mL vials. The k_w term determined

in this manner (Eq. 36) varied from 2 mL/g up to 6 mL/g with an average value of about 4 mL/g.

Measurements of Sorption to Indulin® AT

For the sorption measurements using model lignin precipitates, accurate measures could be made from the solution phase concentration change. In these experiments, the same approach as that for the fiber measurements was used except that triplicate solution phase activity measurements (250 μL), both before the lignin sorbent was added, DPM_i, and after the system had reached equilibrium, DPM_f, were used to determine the distribution coefficients

$$K_d = \frac{\frac{(DPM_i - DPM_f)\, V}{m_l}}{DPM_f} \tag{28}$$

where m_l is the mass of lignin in the sample (oven-dried) and V is the aqueous solution volume. For mass balance trials, the separated lignin material was dissolved in 5 mL of ethylene glycol, a small aliquot (50 μL) was counted in 20 mL of scintillation cocktail at a window setting of 300-670, and corrections were made using the chemical quench curves. The activity recovered was then estimated and compared to that lost by the solution phase during the sorption experiment. Results indicated > 98% recoveries of the isotopes.

Grinding of Pulp Fibers

The effect of fiber surface area was tested by measuring the sorption of model

compounds to kappa number 69.8 fibers which had been dried and ground into powder using a Wiley Mill. Image analysis on the fibers showed that most of the ground fiber particles (> 80%) had lengths of less than 0.1 mm and could be categorized as fines, while none of the unground fibers fell into this category, and the arithmetic average fiber length for the ground fibers (0.09 mm) was more than an order of magnitude lower than that for the unground fibers (1.90 mm). These results indicated that grinding dramatically changed the structure of the fibrous solids, which likely resulted in a substantial increase in surface area. Image analysis data was extracted with a Zeis (Hanover, MD) Axioskop microscope equipped with a CDC (Boyertown, PA) Model I RGB camera, and a Vision Plus-AT® image driver board (Imaging Technology, Bedford, MA). The data was processed with the Optimas™ (Bioscan, Edmonds, WA) 4.0 Image Analysis Program and Microsoft (Remond, WA) Excel 5.0.

Third-Phase Effect Measurements

Lignin colloidal or third-phase solutions were produced by leaching lignin precipitate samples with distilled water. This was done using a pressurized filtration stir cell (Amicon, Beverly, MA) in which the solid phase was retained by a 0.05-μm polycarbonate filter (Poretics, Livermore, CA). The levels of organic carbon (TOC) retained by the aqueous filtrate were determined using a Shizmadzu (Kyoto, Japan) Model TOC-5050 Total Organic Carbon Analyzer. It was found that the level of third-phase material in a pulp slurry correlated with the absorption of light at a wavelength of 276 nm (Fig. 16) determined on a Perkin-Elmer (Norwalk, CT) Model Lambda 4B UV/VIS Spectrophotometer. For studies in which the level of colloidal materials was raised in sorption samples, dilutions of an initial concentrated colloid solution were

used as the aqueous phase. The TOC levels in samples could be calculated from the initial level in the stock solution and checked through light absorption.

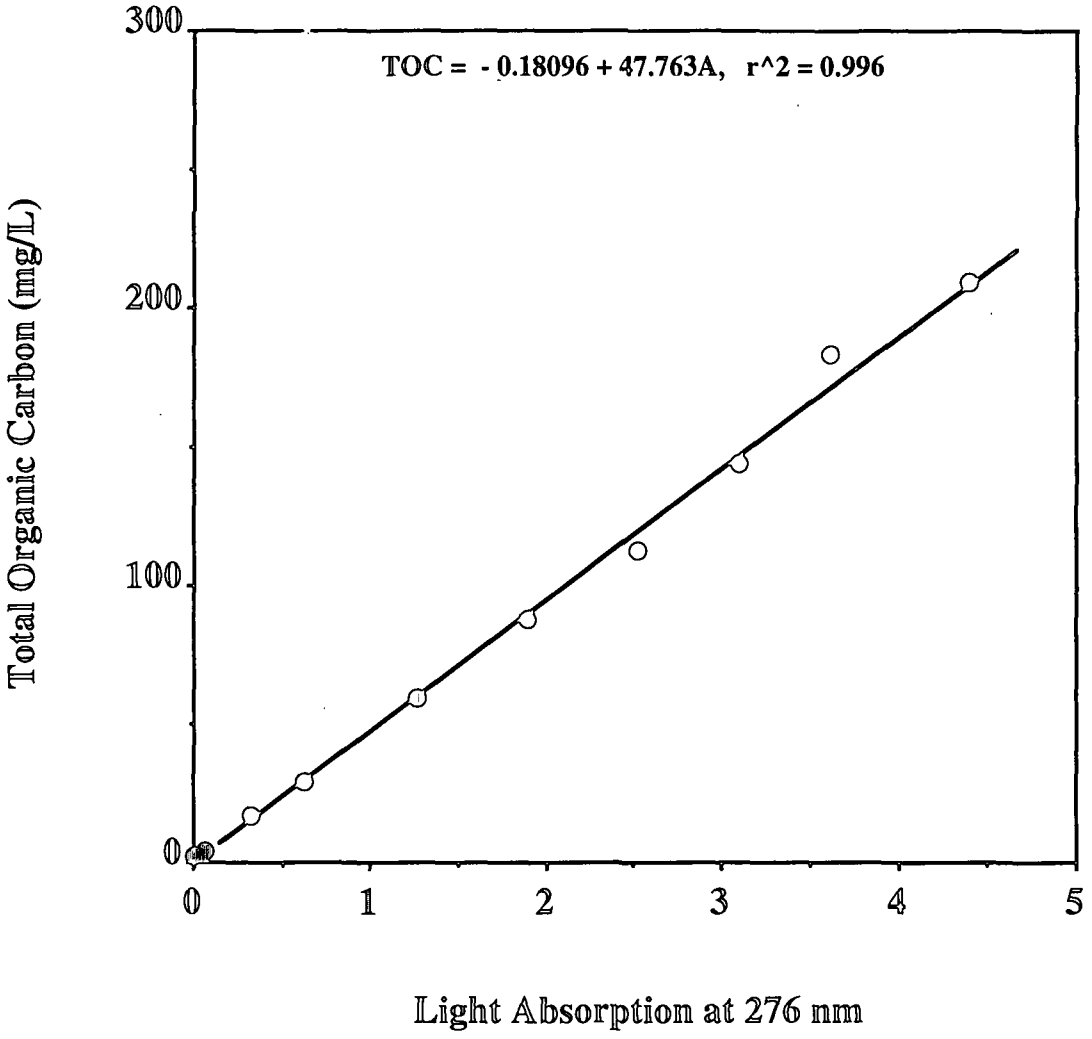


Figure 16. Total Organic Carbon (TOC) levels in aqueous solution vs. light absorption at 276 nm.

Measurements of Sludge Sorption

A primary sludge sample and a clarifier overflow sample (extractive filtrates only) were obtained from a kraft mill with a $DE_{op}DE_pD$ bleaching sequence. Small amounts of formalin were added to both solid and aqueous effluents to quench all biological activity, and the samples were stored at 5°C. A portion of the overflow sample was passed through a 0.05-μm polycarbonate filter (Poretics, Livermore, CA) from a pressurized stir cell (40 psi) and sent to Ecology and Environment, Inc. (Lancaster, NY) for ion analysis, and a dried sludge sample was sent to Econotech (New Westminister, BC, Canada) for ash[62,63] and Klason lignin[64] analysis.

Experiments on sludge included studies with whole sludge and sludge separates (fibers, shives) in either clarifier overflow or pH 7 buffered distilled water. In the study of sludge with the shives removed, the fibers were run either unwashed or after a thorough washing with a pH 9 buffer solution to remove fines and other organic debris. The general procedure for these experiments was to mix a 100-ppb solution of either [^{14}C] 2,4-dichlorophenol or [^{14}C] 2,4,5-trichlorophenol with the sludge samples in 20-mL amber vials capped with Teflon®-lined seals. The samples were mixed for 24 hours, and sorption was determined by the loss of activity from the aqueous phase (Eq. 28). All mass balances indicate > 95% recoveries.

Influent fines were isolated by centrifuging clarifier overflow samples to produce a 500-mg/L solids concentration. A measurement of the solids level of each 500-mL sample was determined by separating the fines from 10 mL-aliquots by vacuum filtration through a preweighed 0.01-μm anodized aluminum filter (Alltech, Deerfield, IL). A seven-fold solids level determination from each of the generated solutions indicated

good reproducibility. FTIR measurements on the recovered fine material indicate it is composed largely of fibrous debris (high levels of both cellulose and lignin). K_d values for the samples were measured by adding either [^{14}C] 2,4-dichlorophenol or [^{14}C] 2,4,5-trichlorophenol to produce a 100-ppb solution, stirring the system for 24 hours, and running liquid scintillation counting on the fines removed through the filtration of 10 mL-aliquots. Isotope recoveries were > 99%.

Kinetics Trials

A 250-ppb aqueous stock solution of 2,4,5-TCP was prepared in a 2000-mL amber volumetric flask and mixed for 24 hours prior to the study. Kappa number 105 softwood fibers were placed in a pH 7.00 aqueous buffer and also mixed for 24 hours prior to the study. All kinetics trials were carried out in 250-mL Erlenmeyer flasks. For mixed samples, 200 mL of the stock solution was added to the flasks which were placed on a magnetic stirrer and stirred with a 2-inch octagonal magnetic stir rod. The initial concentration was measured through the scintillation counting of 100 μL aliquots of the stirred solution. The fibers were separated from the buffer using vacuum filtration and dropped into the solution at time zero. Concentration drops were determined by counting 100 μL from the samples at times determined using a hand-held stop watch accurate to within a hundredth of a second. Samples were pulled as rapidly as possible for the initial 10 minutes (about one per minute) then less frequently until the trial was stopped. Although it took only minutes for the system to reach equilibrium, the samples continued to be drawn for a period of four days for comparison with the unmixed samples. The use of these micro-aliquots produced only a minor drop in the volume of the aqueous phase ($\leq$ 1%), which was considered to be

a constant. For the unmixed samples, the initial concentration was determined, and the fibers separated from the buffer were gently placed into the unmixed solution at time zero. Concentration drops were determined by counting 100 μL-aliquots taken periodically until the system reached equilibrium ($\sim$ four days). Both mixed and unmixed blank samples run without the presence of fibers indicated that there was $< 0.5\%$ loss of solute due to volatilization over the four-day period.

THE EFFECT OF FIBER COMPOSITION AND CHLOROPHENOL IONIZATION ON SORPTION

INTRODUCTION

A processed wood fiber is a composite structure composed mainly of cellulose and lignin. The chemical differences between these components result in significant differences in their ability to interact with water; the polyhydroxyl structure of cellulose provides for strong hydrogen bonding, whereas lignin's phenylpropane units produce relatively hydrophobic regions. For the sorption of nonpolar organics from an aqueous solution, there is strong evidence that variations in the hydrophilicity of a sorbent strongly impact its retention of organic chemicals.[22,65–68] Studies have shown significant reductions and even the elimination of sorption with increasing sorbent polarities. Experiments using cellulose and lignin model particles as sorbents also demonstrate this, with aqueous toluene and trichloroethylene solutes showing a much higher affinity for the lignin particles.[69] This indicates that lignin may dominate the sorption of nonpolar organic species in pulp fibers and fiber solids much in the same way that organic matter dominates sorption in soils and sediments.[30,31] But chlorophenolic compounds are not completely nonpolar species. The presence of an ionizable hydroxyl group creates the potential for both hydrogen bonding and interactions between the compound's ionized form and the fiber surfaces. The impact of the hydroxyl group is difficult to gauge for the neutral form of chlorophenolic compounds. It is generally noted that hydrogen bonding can dramatically increase sorption,[18,70,71] but studies on the aqueous sorption of phenols to various organic sorbents conflict on this issue.[72–75] Some studies report an increase of sorption with greater sorbent oxidation levels while others report either no effect or a decrease. Possibly, any sorp-

tion enhancement due to the creation of specific bonding sites is balanced by the decreased sorption which results from the sorbent's increased interaction with the aqueous phase.

For ionized chlorophenols, the effect of the charged functional group on sorption is expected to be significant. Ionized organic compounds are much more water soluble than their conjugate acids. Measurements of organic-phase-water distributions for various organic acids indicate that the neutral form dominates partitioning for an aqueous pH which is less than about 2 units above the solute's pK_a value.[75,76] Similar results are found for the solid-water distribution of chlorophenols indicating that only the neutral form needs to be considered under these conditions.[49] But, in situations where the ionic form of the chlorophenol is the dominant form in solution, some studies have indicated that the sorption of the organic ion cannot be neglected.[49,77,78] Pentachlorophenol sorption to soils has been shown to remain strong even after the compound is completely ionized,[78] and studies of other chlorophenol's retention by soils and sediments demonstrate that chlorophenolate sorption is significant.[49,77]

THEORY

Contributions to the Fiber-Water Distribution Coefficient

The distribution coefficient is defined (Eq. 2) as the ratio between the solute concentration that is retained by the solid or fiber phase, C_s, and the solute concentration that remains in the aqueous solution, C_w. Pulped wood fibers separated from an aqueous solution can retain a significant volume of water which is held through capillary forces in the void regions of a fibrous network and within the individual fiber's cell

walls and lumen (hallow region in the center of the fiber).[79–82] Thus, C_s can be divided into three independent contributions which include the mass of solute retained by cellulose, s_c, lignin, s_l, and the solute which is retained in the water of the solids, s_w, divided by the oven-dried mass of fiber, $m_{o.d.}$

$$C_s = \frac{s_c + s_l + s_w}{m_{o.d.}} \tag{29}$$

Equation 29 can be rewritten in terms of the oven-dried mass fractions and solute concentrations in cellulose and lignin, f_c, f_l, and C_c, C_l, respectively

$$C_s = f_c\, C_c + f_l\, C_l + \frac{s_w}{m_{o.d.}} \tag{30}$$

By dividing through by the concentration of the solute in the aqueous phase, C_w, the fiber-water distribution coefficient can be expressed in terms of sorption contributions from the cellulose-water, K_c, and lignin-water, K_l, distribution coefficients as

$$K_d = f_c\, K_c + f_l\, K_l + \frac{\frac{s_w}{m_{o.d.}}}{C_w} \tag{31}$$

Assuming the water held by the fiber phase is similar to the aqueous solution it is separated from, the mass of solute in the fiber water can be expressed in terms of the volume of water retained, V_{fw}, and the concentration of the solute in the aqueous solution, C_w,

$$s_w = V_{fw}\, C_w \tag{32}$$

Since the consistency of the fiber phase, C_f, is defined as

$$C_f = \frac{m_{o.d.}}{mass\ wet\ fiber} \tag{33}$$

V_{fw} can be written in terms of C_f as

$$V_{fw} = \frac{1}{\rho}\left[\frac{1}{C_f} m_{o.d.} - m_{o.d.}\right] \tag{34}$$

where ρ is the density of the aqueous solution. Substituting Eqs. 32 and 34 into Eq. 31 yields

$$K_d = f_c\, K_c + f_l\, K_l + \frac{1}{\rho}\left[\frac{1 - C_f}{C_f}\right] \tag{35}$$

The last term in this equation can be thought of as the water retention coefficient, k_w, defined as

$$k_w = \frac{1}{\rho}\left[\frac{1 - C_f}{C_f}\right] \tag{36}$$

The mass fraction of lignin in a pulp fiber, f_l, is typically reported within the paper

industry by a kappa number, η. By definition, kappa number is the volume of 0.1N potassium permanganate solution consumed by one gram of moisture-free pulp under the conditions specified by the test method.[58] The permanganate oxidizes the non-cellulosic or lignin portion of the pulp fibers. The kappa number is related to the lignin mass fraction through the equation[58]

$$f_l = 0.0015\,\eta \tag{37}$$

The substitution of Eq. 37 as well as $(1 - f_l)$ for f_c into Eq. 35 results in a linear relation between kappa number and measured fiber-water distribution coefficients for aqueous organic compounds

$$K_d = \frac{1}{\rho}\left[\frac{1 - C_f}{C_f}\right] + K_c + 0.0015\,(K_l - K_c)\,\eta \tag{38}$$

Ionization: The Sorption of Chlorophenolates

When ionization occurs, the concentration of chlorophenols sorbed to the fibers may include the neutral as well as the ionized form of the compound (chlorophenolates). As discussed earlier, sorption of chlorophenolates to natural organic matter is small in comparison to the sorption of their neutral form. This allows it to be neglected in situations where only a small fraction of a compound is ionized. Under these conditions, sorption can be estimated as the fraction of the compound in the neutral form, α, multiplied by the neutral compound's distribution coefficient, K_d^0

$$K_d = k_w + \alpha K_d^0 \tag{39}$$

where α is calculated using the compound's pK_a and the pH of the aqueous phase

$$\alpha = \frac{1}{1 + 10^{(pH - pK_a)}} \tag{40}$$

Substitution of Eq. 39 into Eq. 38 gives

$$K_d = \frac{1}{\rho}\left[\frac{1 - C_f}{C_f}\right] + \alpha\left[K_c^0 + 0.0015\,(K_l^0 - K_c^0)\,\eta\right] \tag{41}$$

It should be noted that in Eq. 41, K_c^0 and K_l^0 are used to represent the cellulose-water and lignin-water distribution of the solute's neutral form.

RESULTS AND DISCUSSION

The equations developed in this chapter assumed that K_d is independent of solute concentration, so it is important to establish that isotherms in the typical concentration range of chloro-organics in bleaching effluents[29] can be fit accurately with a linear model. Figures 17 and 18 are the isotherms for the sorption of 2,4-DCP and 2,4,5-TCP to kappa number 69.8 softwood fibers. For these measurements, the chlorophenol concentration was varied from less than 1 ppb to more than 1 ppm. The isotherms are clearly linear (i.e., K_d is independent of chlorophenol concentrations).

It should also be noted that the solids effect[21,48,83–89] did not appear in these experiments. As will be discussed in Chapter 5, measurements covering three orders of magnitude in sorbent concentrations showed no significant change in K_d.

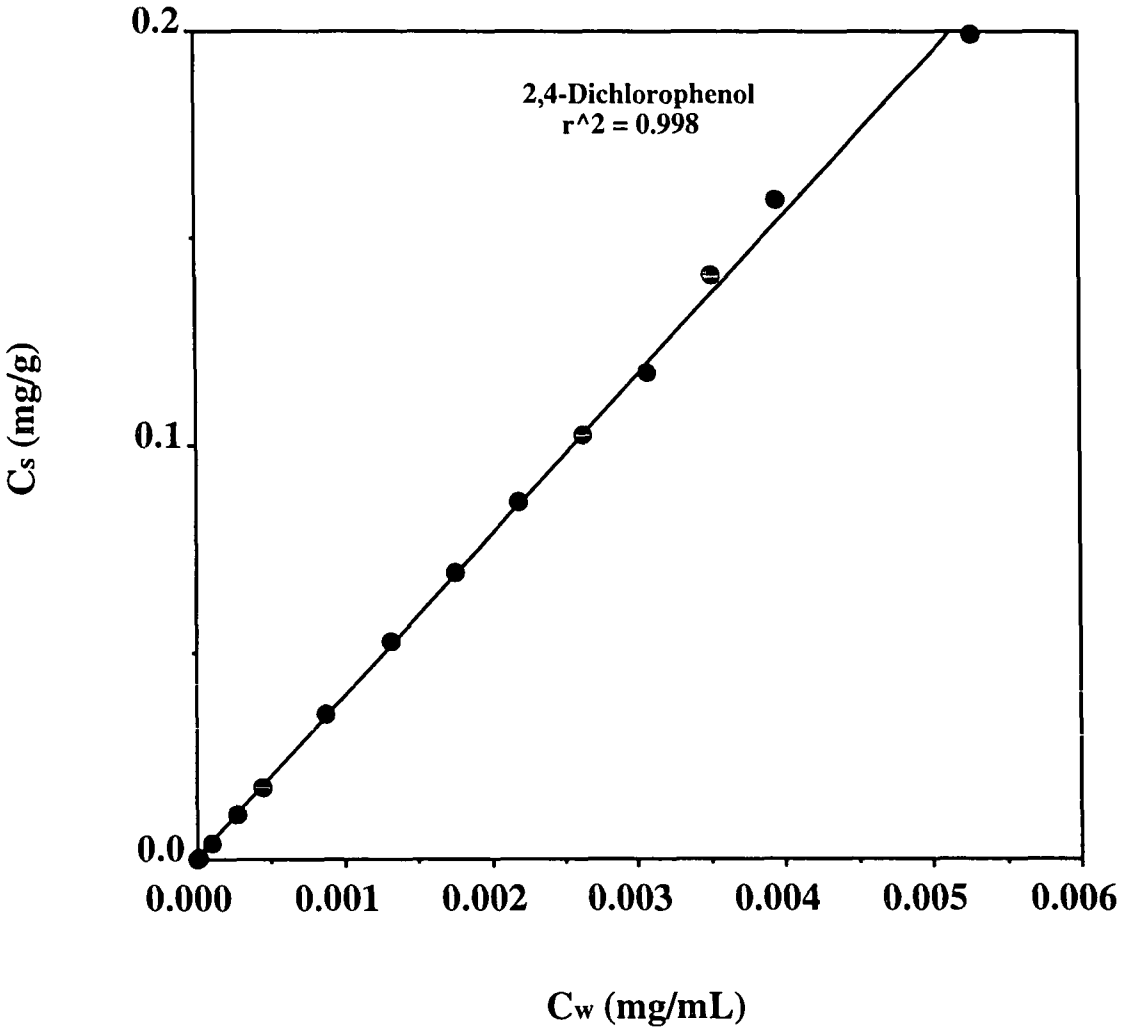


Figure 17. Isotherms for the sorption of 2,4-dichlorophenol to kappa number 69.8 softwood fibers at 25°C and pH of 7.00.

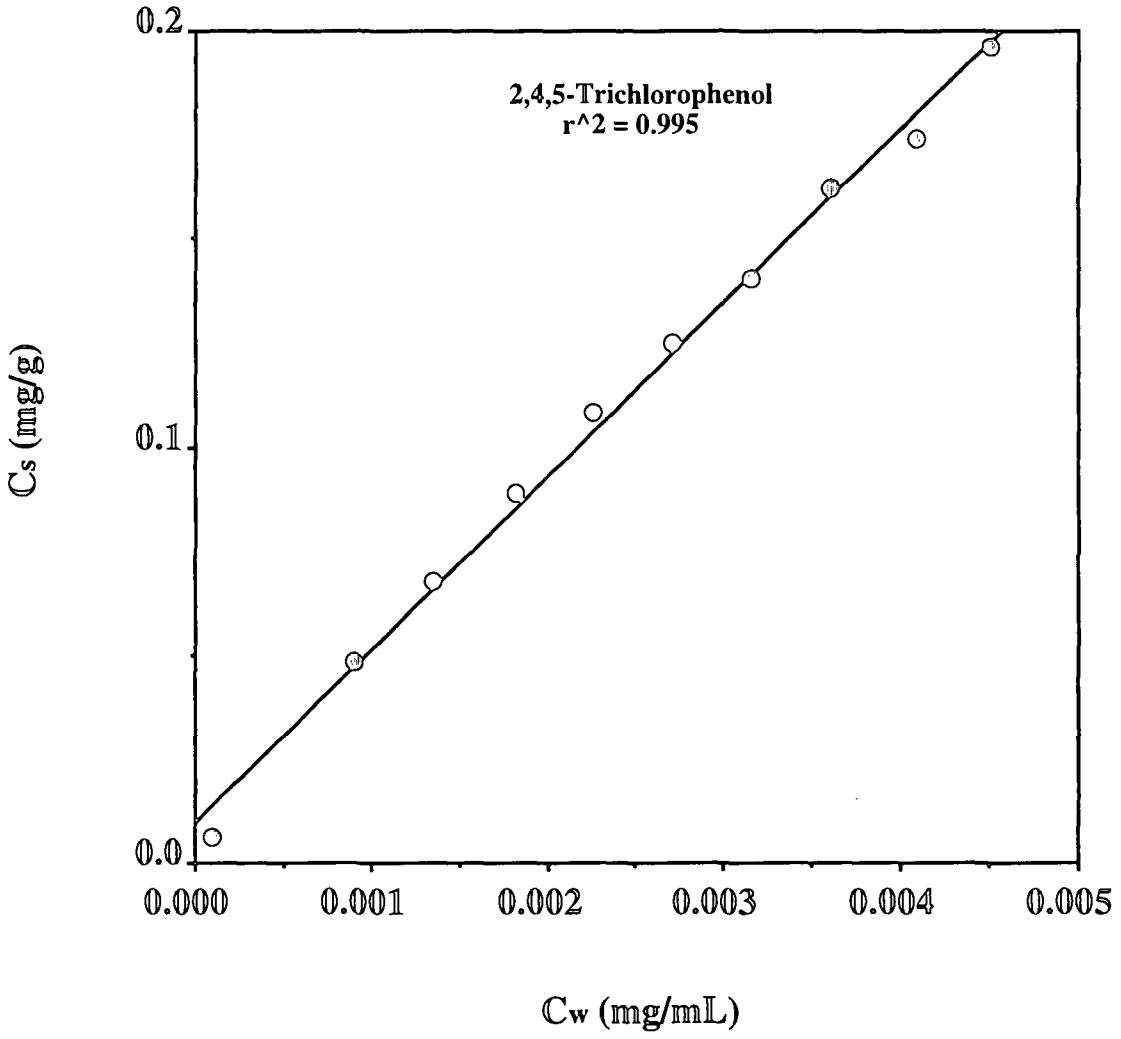


Figure 18. Isotherms for the sorption of 2,4,5-dichlorophenol to kappa number 69.8 softwood fibers at 25°C and pH of 7.00.

pH Dependency and Chlorophenolate Sorption

Figure 19 shows the distribution of 2,4,5-TCP between distilled water and kappa number 105 softwood pulp fibers as a function of pH. The curve represents the sorption predicted for the compound by Eqs. 39 and 40 using the measured k_w value of 4 mL/g and the measured distribution coefficient, K_d^0. The excellent fit in Fig. 19 indicates that the ionized form of the 2,4,5-TCP compound does not sorb, at least not under the low ionic strength conditions used for these measurements. Figures 20 and 21 further confirm these results with Fig. 20 plotting the sorption of 2,4,5-TCP to kappa number 23.9 softwood fibers and Fig. 21 plotting the sorption of both 2,4-DCP and 2,4,5-TCP to a kappa number 69.8 softwood pulp as a function of pH. Figure 21 also shows an interesting situation in which the sorption of the trichlorophenol compound, which typically has the higher sorption, drops below that for the dichlorophenol in the pH range of about 7.7 to 9. For a bleached kraft paper mill, the primary clarifier influent will typically have a pH of around 8 (extractive effluents). From Fig. 21, it is apparent that any prediction of a chlorophenolic compound's distribution in bleaching effluents will have to take into account the effects of ionization on sorption.

Figure 22 shows the fit for the sorption of both the di- and trichlorophenol to kappa number 69.8 softwood fibers. Here, the measured distribution coefficients were plotted as a function of α (Eq. 40) which, according to Eq. 39, should produce linear fits with the slopes providing estimates of K_d^0. Data were collected in the pH range of 6 to about 10 to be more representative of the conditions found in bleaching effluents and the primary clarifier. As demonstrated, even when the chlorophenolates dominate at high pH, the data are fit quite well with a line. Slope values for 2,4-DCP and 2,4,5-TCP sorption are 42.2 and 119 mL/g, respectively, which match the K_d values measured at

low pH in Fig. 21. These results conflict with the work of others on the role of ionized phenols in the sorption to soil and sediment samples.[49,77,78] As was noted earlier, it has been argued that while neutral chlorophenols dominate sorption, contributions of the ionized form are significant at high pH. This may be due to the sorption of the conjugate base to the mineral fraction of the soil and sediment samples or to the fact that most of the data in these studies included highly chlorinated phenols which remain relatively hydrophobic even after ionization. But for the sorption of the di- and trichlorinated phenols to pulp fibers, it is clear that the ionized form plays no role in sorption within the 2 - 12 pH region, indicating the only mechanism of concern is the water-solid distribution of the neutral compound.

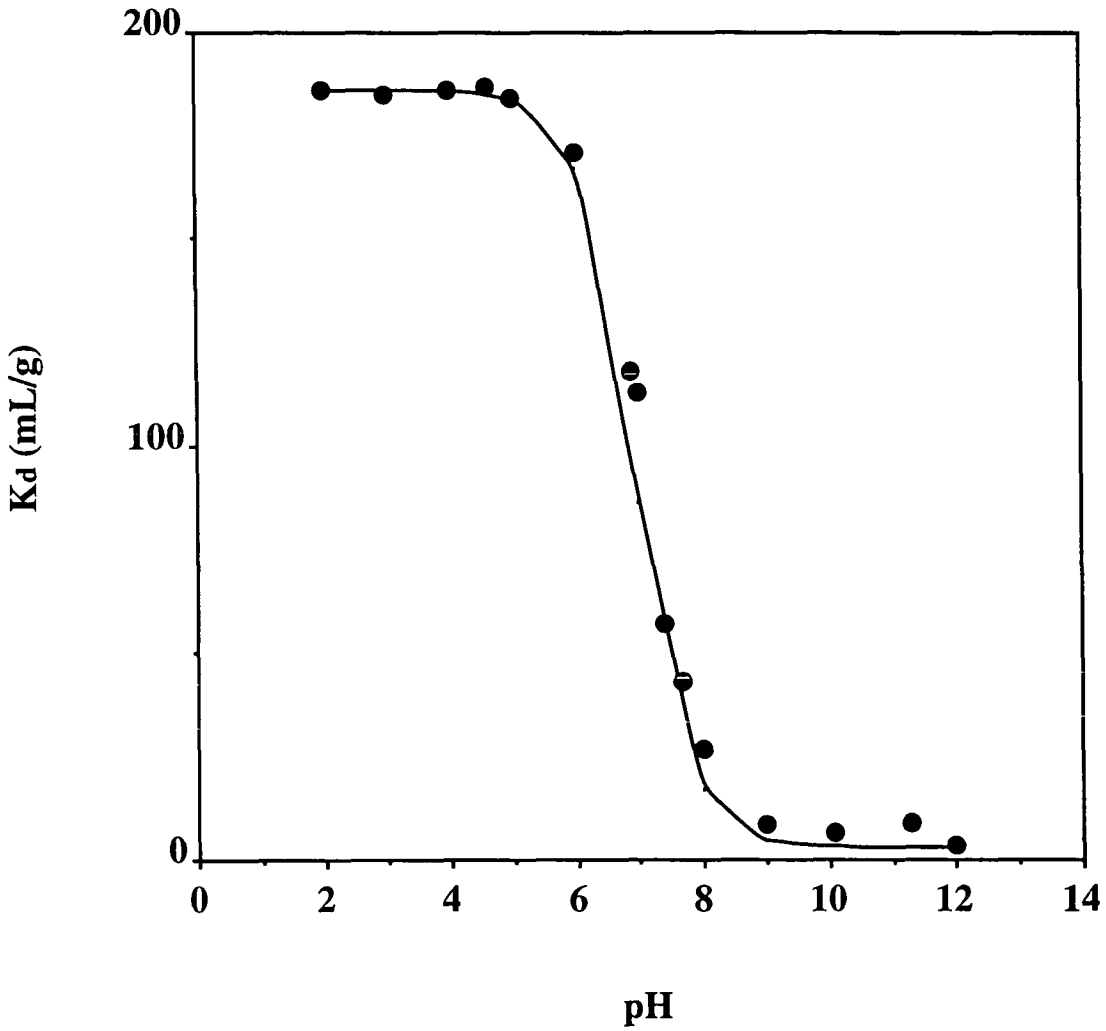


Figure 19. Sorption of 2,4,5-trichlorophenol to kappa number 105 softwood fibers. The solid curve is a plot of Eq. 39.

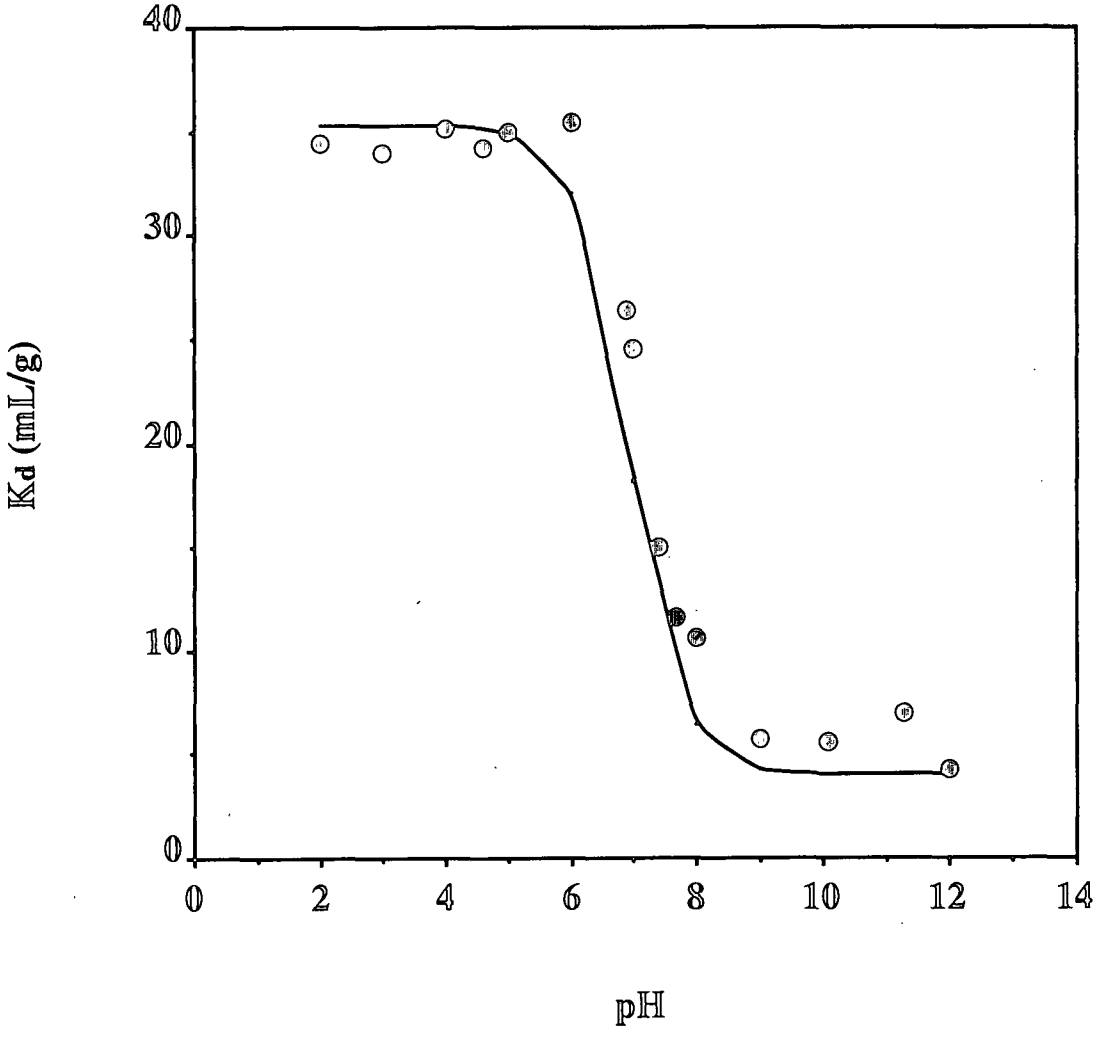


Figure 20. Sorption of 2,4,5-trichlorophenol to kappa number 23.9 softwood fibers.

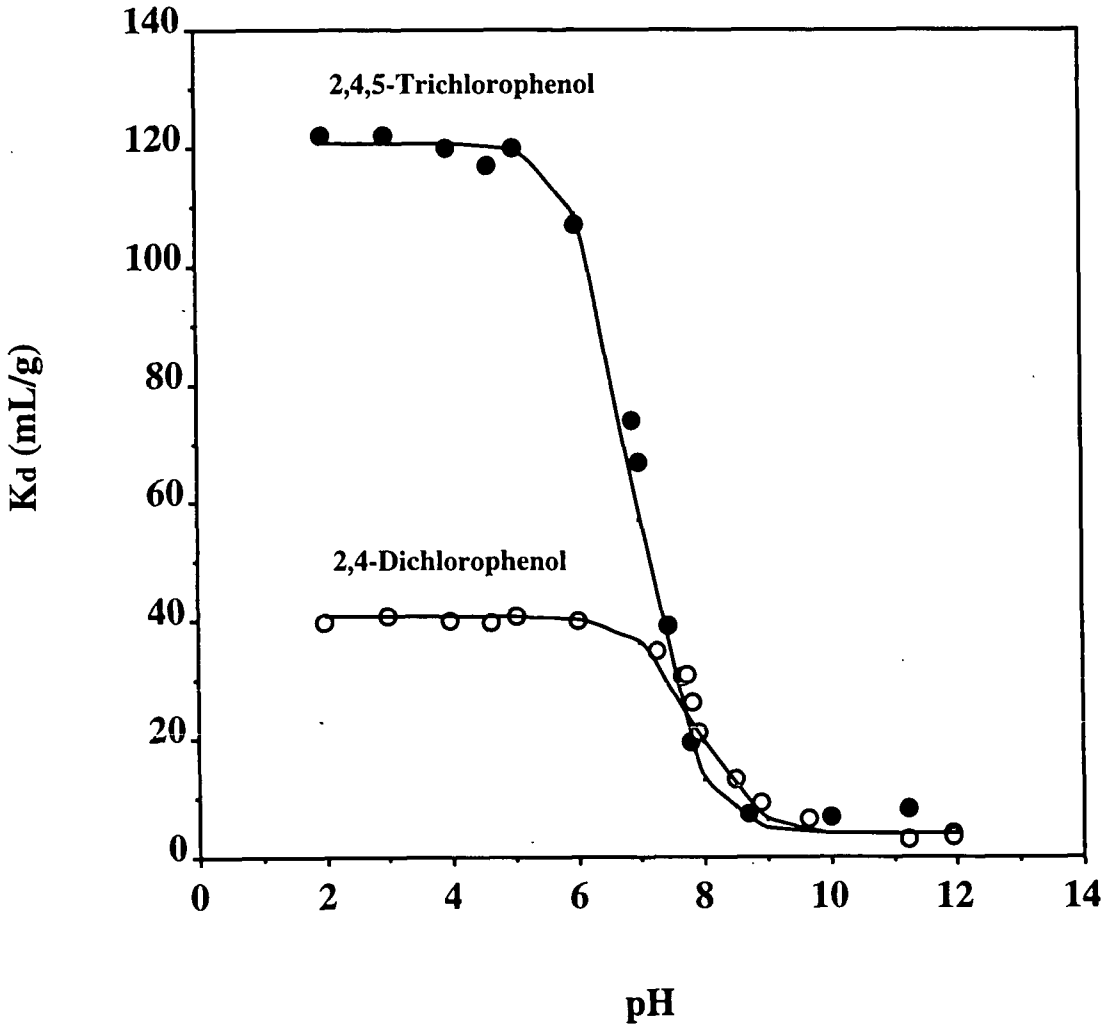


Figure 21. Sorption of 2,4-dichlorophenol and 2,4,5-trichlorophenol to kappa number 69.8 softwood fibers.

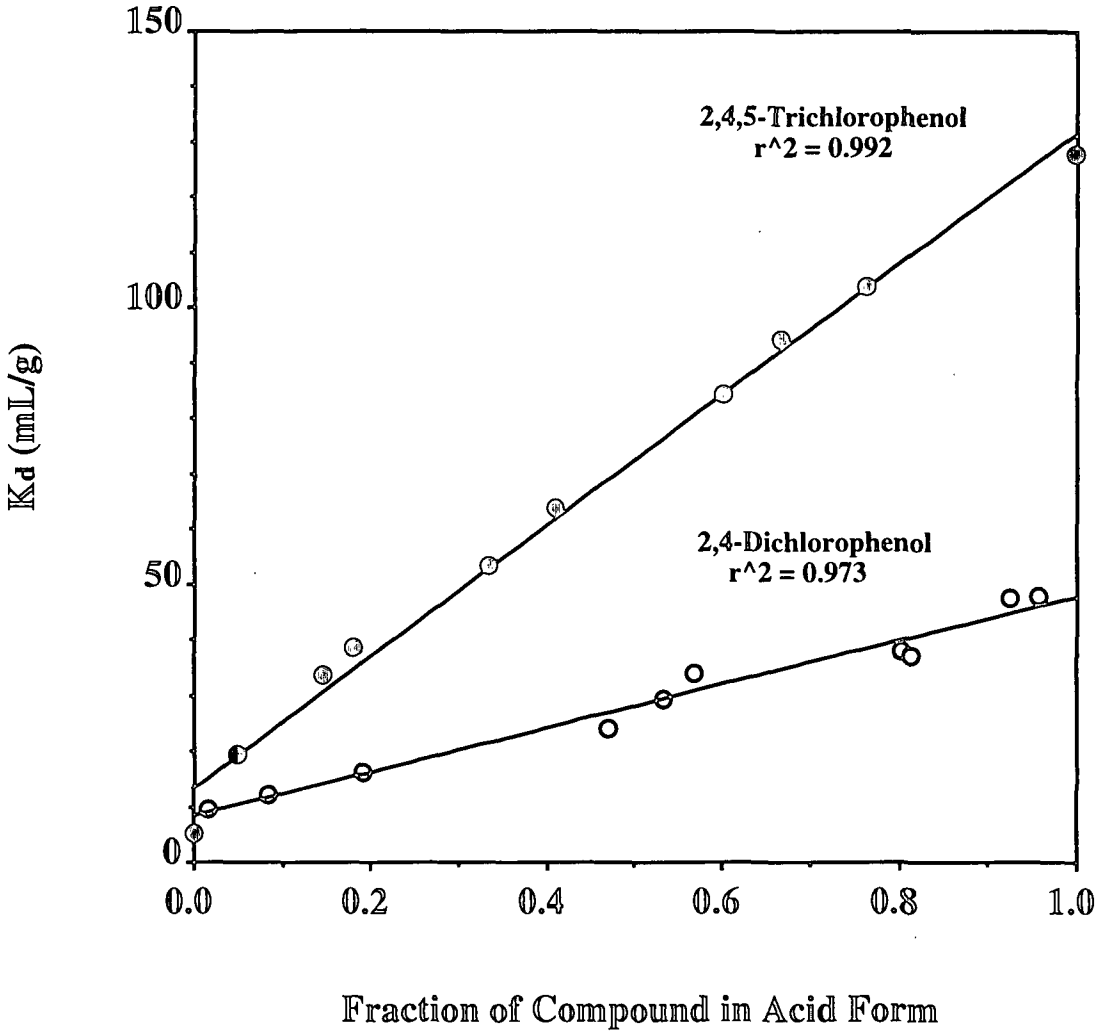


Figure 22. Sorption of 2,4-dichlorophenol and 2,4,5-trichlorophenol to kappa number 69.8 softwood fibers as a function of the chlorophenol fraction in its acid form.

The Lignin-Water Distribution Coefficient

Figures 23 through 29 plot the sorption of both 2,4-DCP and 2,4,5-TCP as a function of the level of ionization of the chemicals (fraction or compound in acid form). These plots are examples of the data collected for a full range of lignin content pulps starting with cotton linters and ending with kappa number 105 softwood fibers. By plotting the data in this fashion, a comparison of the sorption for the di- and trichlorophenol compounds can be made at the same level of ionization. In each case there is a significantly higher sorption for the trichlorophenol over the dichlorophenol. The figures also demonstrate the importance of lignin in the retention process. A steady increase in K_d (for the neutral compound) is found with increasing lignin, and sorption to the lignin precipitates is more than two orders of magnitude greater than the sorption to the cotton linters for both compounds (Table 4). This indicates that the cellulose-water distribution coefficient, K_c^0, in Eq. 41 can be neglected; i.e.,

$$K_d \;=\; k_w \;+\; 0.0015\,\eta\,\alpha\,K_l^0 \;\approx\; \alpha\,f_l\,K_l^0 \qquad (42)$$

Here, k_w is neglected, and f_l replaces the estimate of lignin mass fraction based on the fibers' kappa number. Figures 30 and 31 plot fiber-water K_d vs. kappa number at two different pH levels for both 2,4-DCP and 2,4,5-TCP, respectively. Figure 31 again demonstrates the inversion of sorption between the di- and trichlorophenol under alkaline conditions where the higher acidity of the trichlorophenol offsets its higher K_d^0. The K_l^0 values estimated from the slopes using Eq. 42 are 360 mL/g and 1200 mL/g for 2,4-DCP and 2,4,5-TCP, respectively. These are consistent with the measured K_l^0 values for the model lignin material (Table 4). This does not automatically imply

that the lignin precipitated from black liquor has the same sorption properties as lignin in fibers, but it does provide strong evidence that lignin materials provide a more stable environment than cellulose materials for the model chemicals.

Table 4. Measured distribution coefficients for the sorption of 2,4-dichlorophenol and 2,4,5-trichlorophenol to pulped wood fibers, cellulose, and lignin model particles.

kappa number	K_d^0 (mL/g)		K_l^0 (mL/g)	
	2,4-DCP	2,4,5-TCP	2,4-DCP	2,4,5-TCP
0	0.343	1.67	0	0
4.93	2.34	4.19	316	566
23.9	15.7	33.6	438	937
32.3	20.4	55.8	421	1152
69.8	39.3	118	375	1127
83.7	47.1	160	375	1274
105	57.5	205	365	1302
lignin precipitates			340	1200

Thus, Eq. 42 appears to provide a good approximation of the fiber-water distribution for chlorophenols and probably also for other organic compounds based on the fiber's lignin content, the compound's pK_a, the solution pH, and the lignin-water distribution coefficient. Except for K_l^0, all of these variables can be found in the literature or predicted. Given that sorption is driven by solute hydrophobicity, it is expected that K_l^0 can be estimated from a linear free-energy relationship.[21,85] Figure 32 plots measured log K_l^0 values of four compounds versus the log of their octanol-water distribution coefficients, log K_{ow}. Values for trichloroethylene and toluene were

taken from a study[69] that used the same model lignin material used in this study. Although the plot combines two sets of data collected under different experimental protocols, the resulting equation

$$\log K_l^0 = 0.95 \log K_{ow} - 0.48 \quad (43)$$

shows a strong correlation and provides an estimate of K_l^0 for organic compounds.

Before leaving this topic, a few comments are necessary on the effect of lignin oxidation on sorption. Published analysis of residual lignin in unbleached and bleached kraft pulps indicates that bleaching increases the concentration of carboxylic groups and drops the concentration of methoxy components, as well as the C/O ratio overall.[90] The effect of these changes in lignin on the sorption of organics is difficult to predict. If the dramatic differences in sorption behavior between cellulose and lignin are caused by the ability of cellulose to interact strongly with water, then the increased oxidation levels would be expected to drop sorption, but, if the sorption process is viewed as a phase distribution process, oxidation may have little impact. The increased oxidation of the lignin should only slightly increase the activity coefficients of the sorbed solutes which are expected to be close to 1, and thus, change K_d only slightly.

The last column of Table 4 lists K_l^0 calculated using Eqs. 37 and 42. All fiber samples listed are brownstock samples with the exception of the cotton linters and kappa number 4.93 softwood fibers which came from the second stage of a DE_oDE_pD sequence. Given that measurements for 2,4-DCP were obtained later in this experimental study which provided time to practice and refine the experimental technique,

it is expected these values are the more accurate measurements. With this in mind, a significant drop in lignin-water sorption does not appear to accompany increased delignification levels for the brownstock fibers, but there does exist a K_l^0 drop for the bleached fibers. To further explore this result, Klason lignin levels were again measured using TAPPI Standard Method T 222 om-88.[64] This method measures the amount of lignin (corrected for ash content) which does not dissolve in a 72% sulfuric acid solution. For unbleached softwood pulps, the insoluble fraction composes more than 99.5% of the total lignin mass, but for semi-bleached pulps this fraction can drop to less than 50%. Insoluble lignin tests on the kappa number 23.9 (brownstock) and 4.93 (semi-bleached) indicated lower lignin levels, which resulted in higher calculated K_l^0 values of 561 and 1376 mL/g for 2,4-DCP and 1200 and 2465 mL/g for 2,4,5-TCP, respectively. Thus, this alternative approach to quantify f_l produces K_l^0 values for the kappa number 23.9 fibers which are consistent with values measured for other brownstock fibers. But, for the bleached fibers, where the insoluble lignin may compose less than 50% of the total lignin content, the estimated sorption is more than double of what was calculated using kappa number to quantify the lignin content, indicating that both the insoluble lignin as well as the highly oxidized soluble fraction participate in the retention of model chemicals. But this conclusion is by no means definite; the accuracy of K_d values and lignin content measurements become relatively poor at low lignin levels, making it difficult to make accurate K_l^0 estimates. The effect of lignin oxidation on sorption is an interesting subject from a mechanistic standpoint and would make a good topic for future studies.

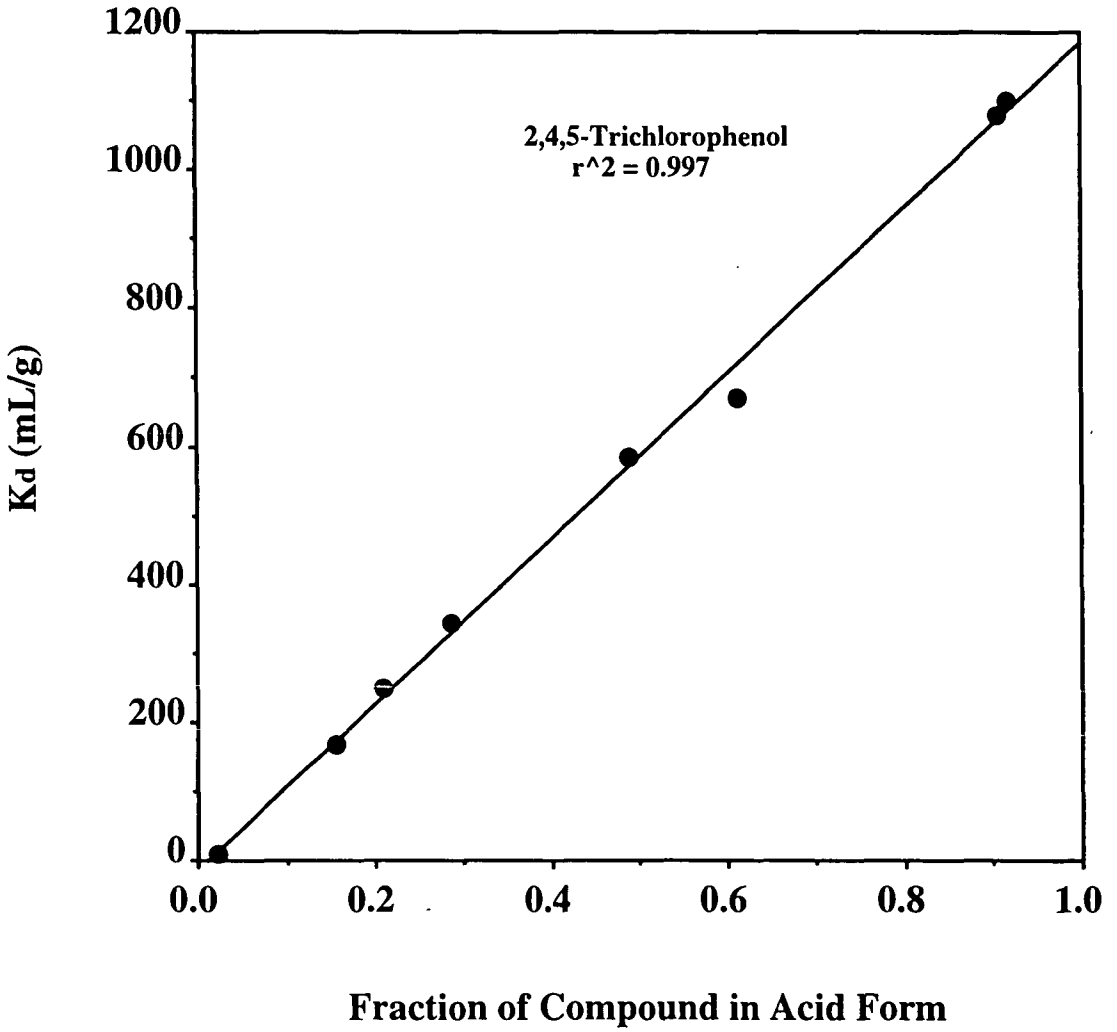


Figure 23. Sorption of 2,4,5-trichlorophenol to model lignin material as a function of the chlorophenol fraction in its acid form.

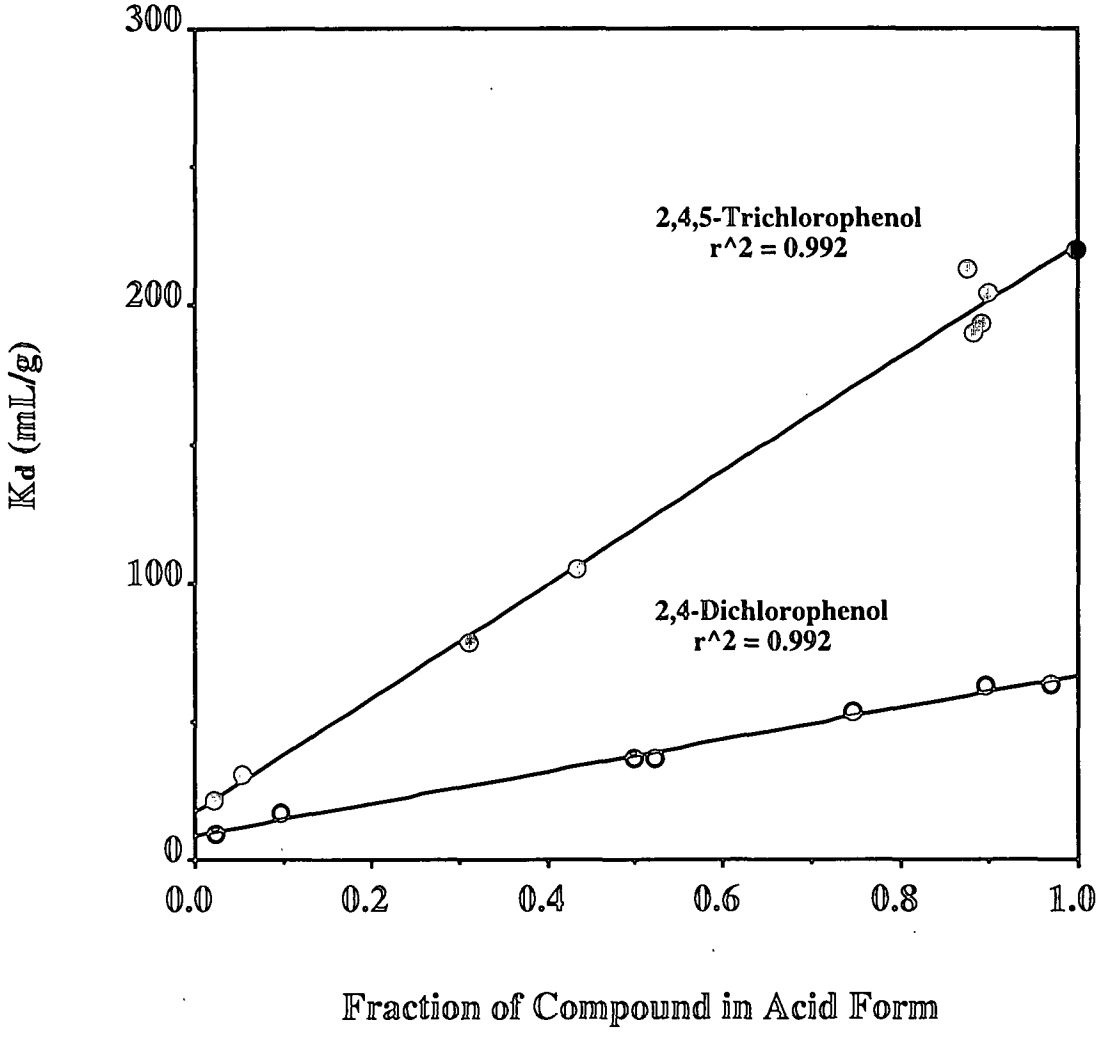


Figure 24. Sorption of 2,4-dichlorophenol and 2,4,5-trichlorophenol to kappa number 105 softwood fibers as a function of the chlorophenol fraction in its acid form.

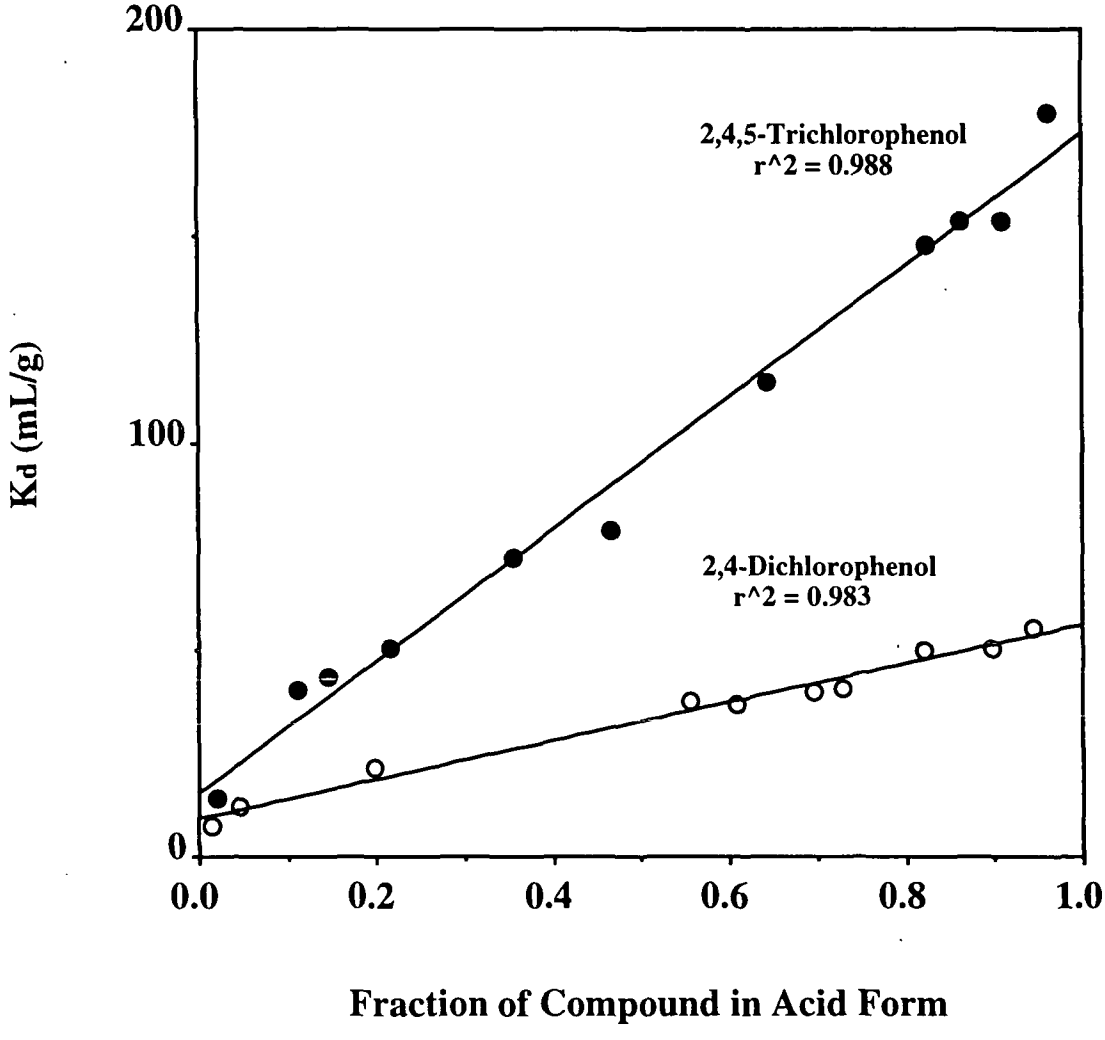


Figure 25. Sorption of 2,4-dichlorophenol and 2,4,5-trichlorophenol to kappa number 83.7 softwood fibers as a function of the chlorophenol fraction in its acid form.

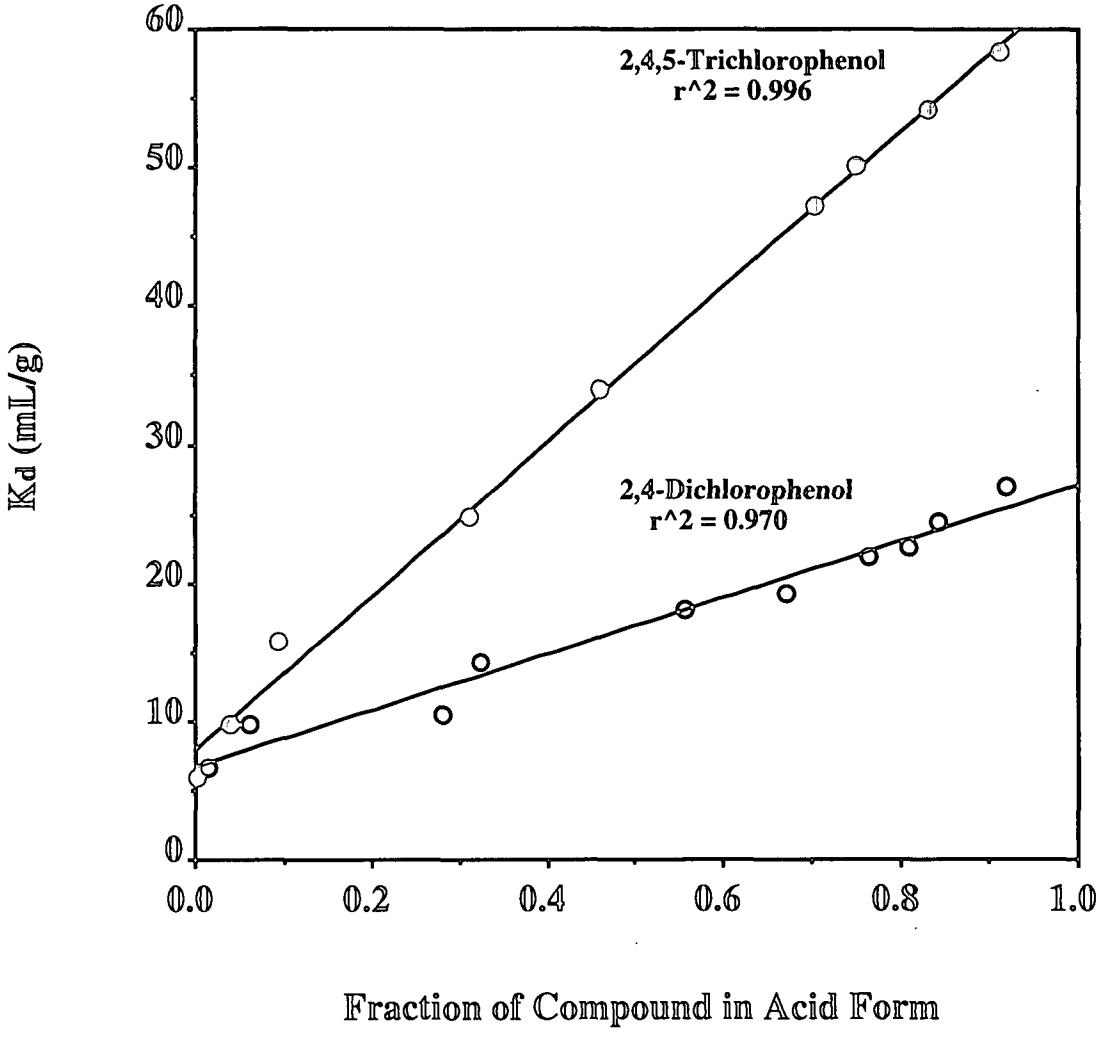


Figure 26. Sorption of 2,4-dichlorophenol and 2,4,5-trichlorophenol to kappa number 32.3 softwood fibers as a function of the chlorophenol fraction in its acid form.

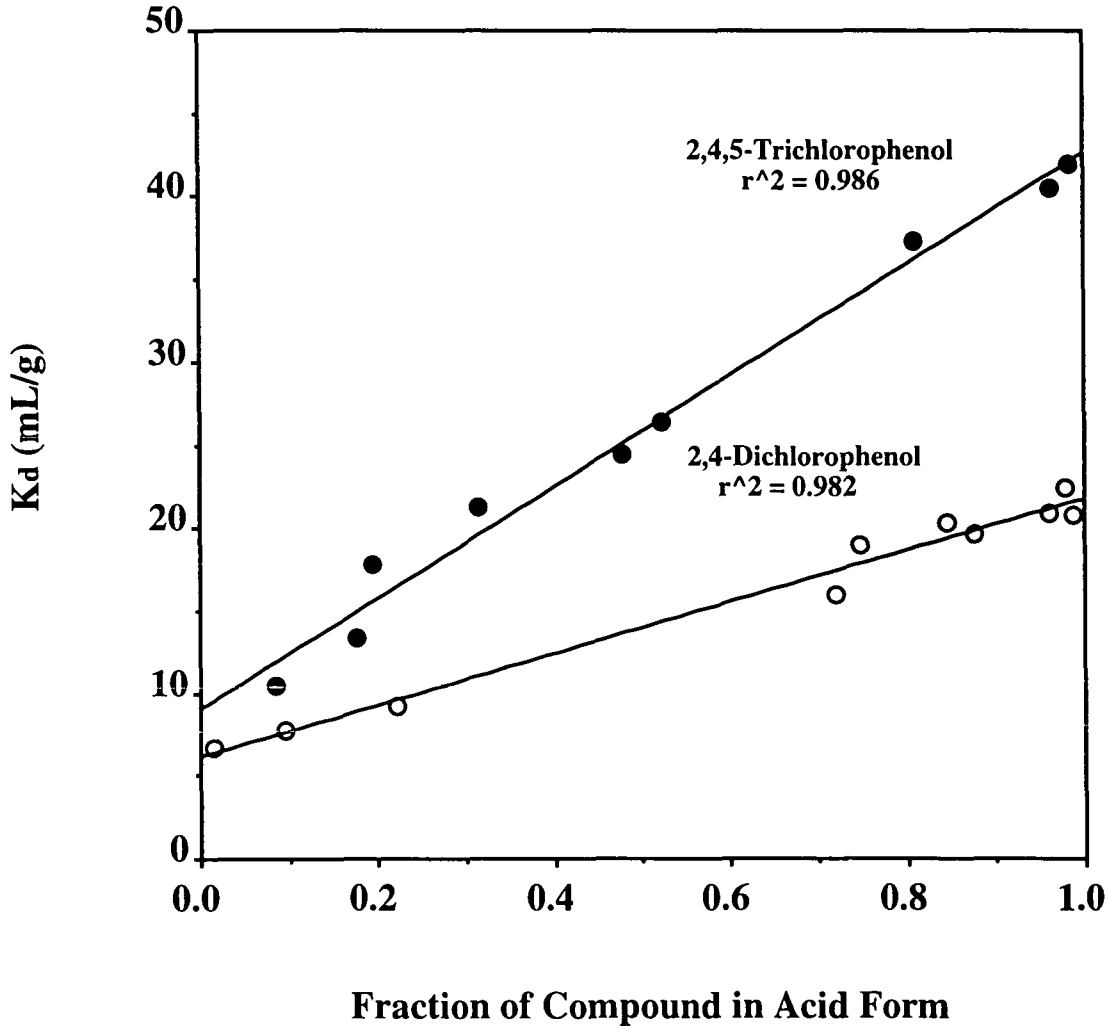


Figure 27. Sorption of 2,4-dichlorophenol and 2,4,5-trichlorophenol to kappa number 23.9 softwood fibers as a function of the chlorophenol fraction in its acid form.

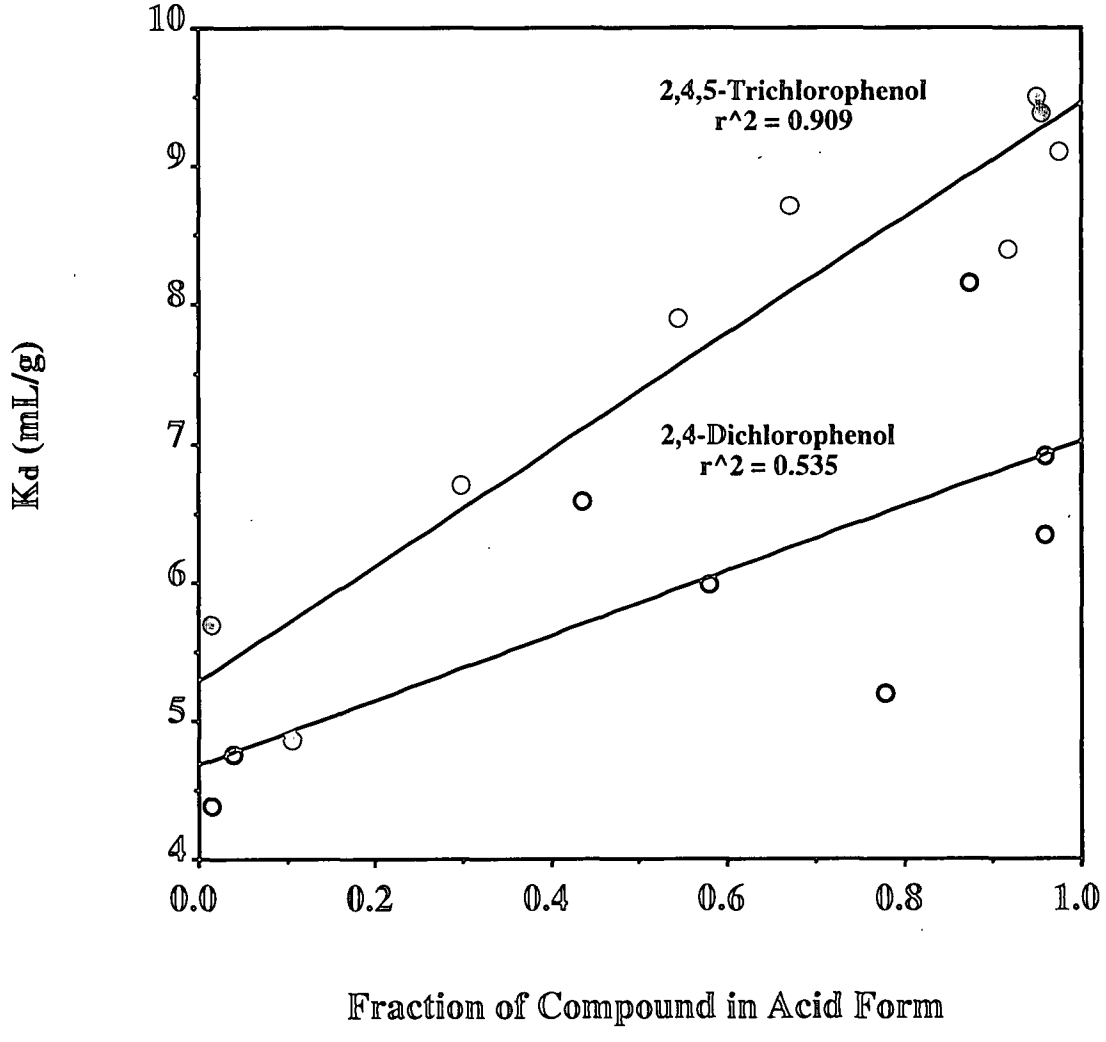


Figure 28. Sorption of 2,4-dichlorophenol and 2,4,5-trichlorophenol to kappa number 4.93 softwood fibers as a function of the chlorophenol fraction in its acid form.

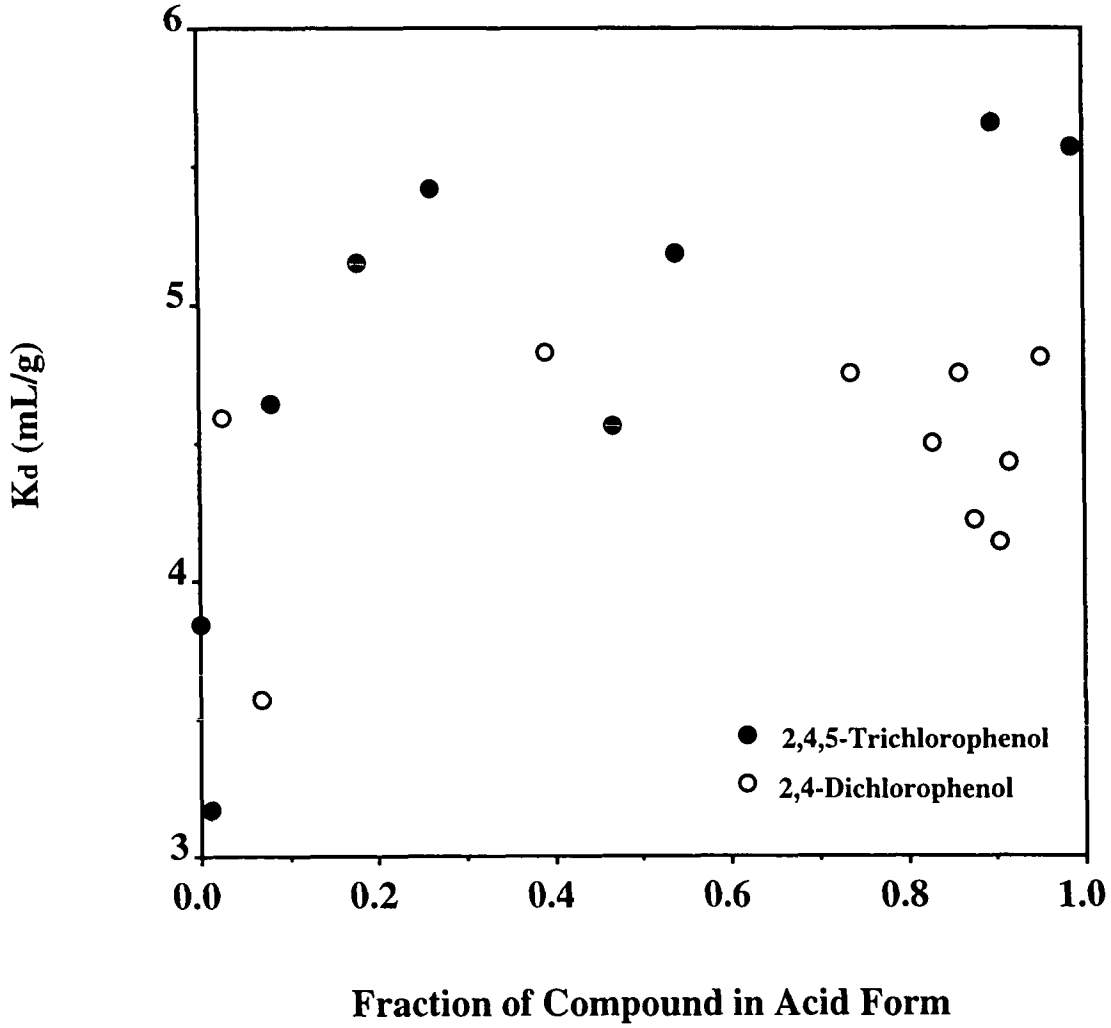


Figure 29. Sorption of 2,4-dichlorophenol and 2,4,5-trichlorophenol to cotton linter fibers as a function of the chlorophenol fraction in its acid form.

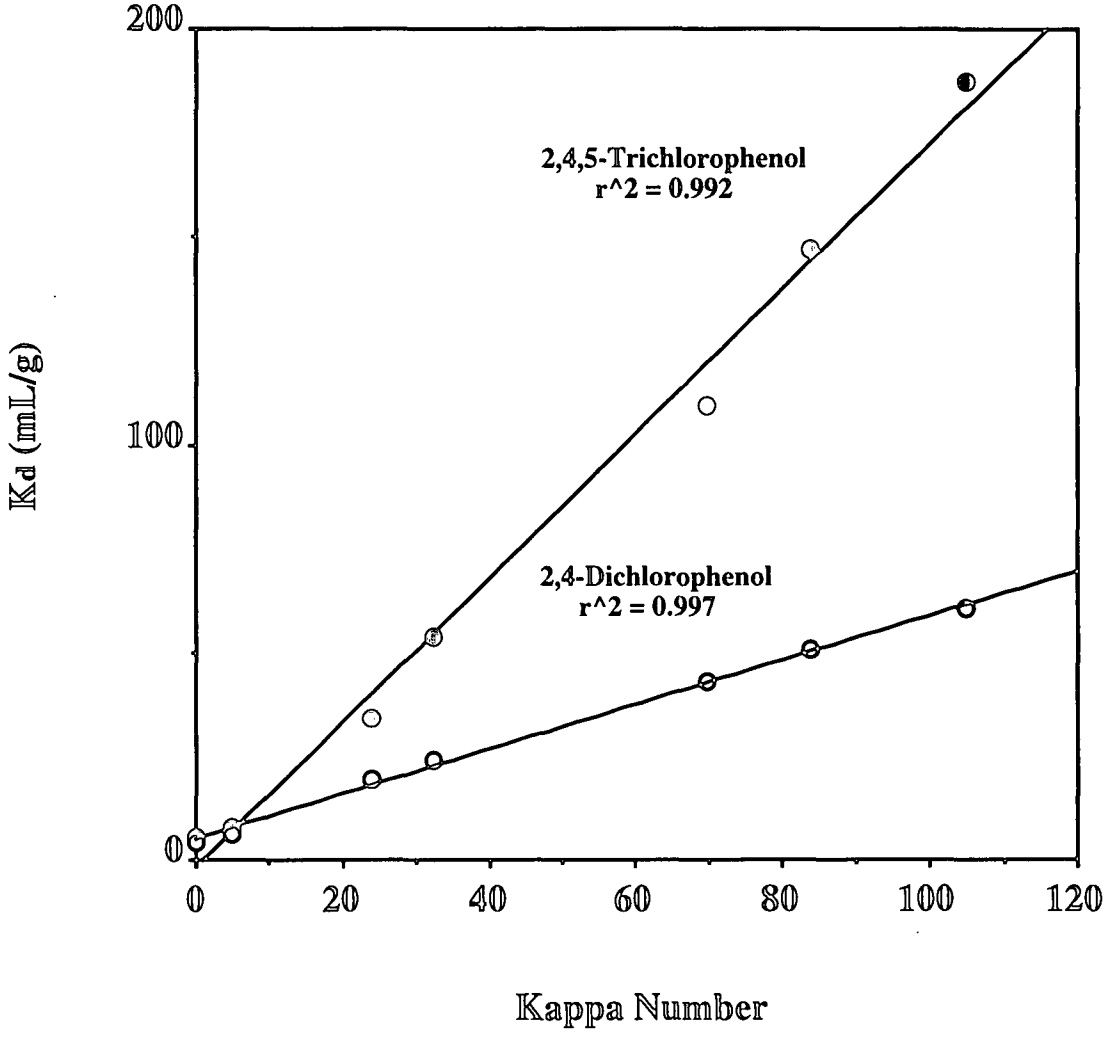


Figure 30. Fiber-water distribution coefficients for 2,4-dichlorophenol and 2,4,5-trichlorophenol versus the kappa number of the softwood fiber sorbents at pH of 6.00.

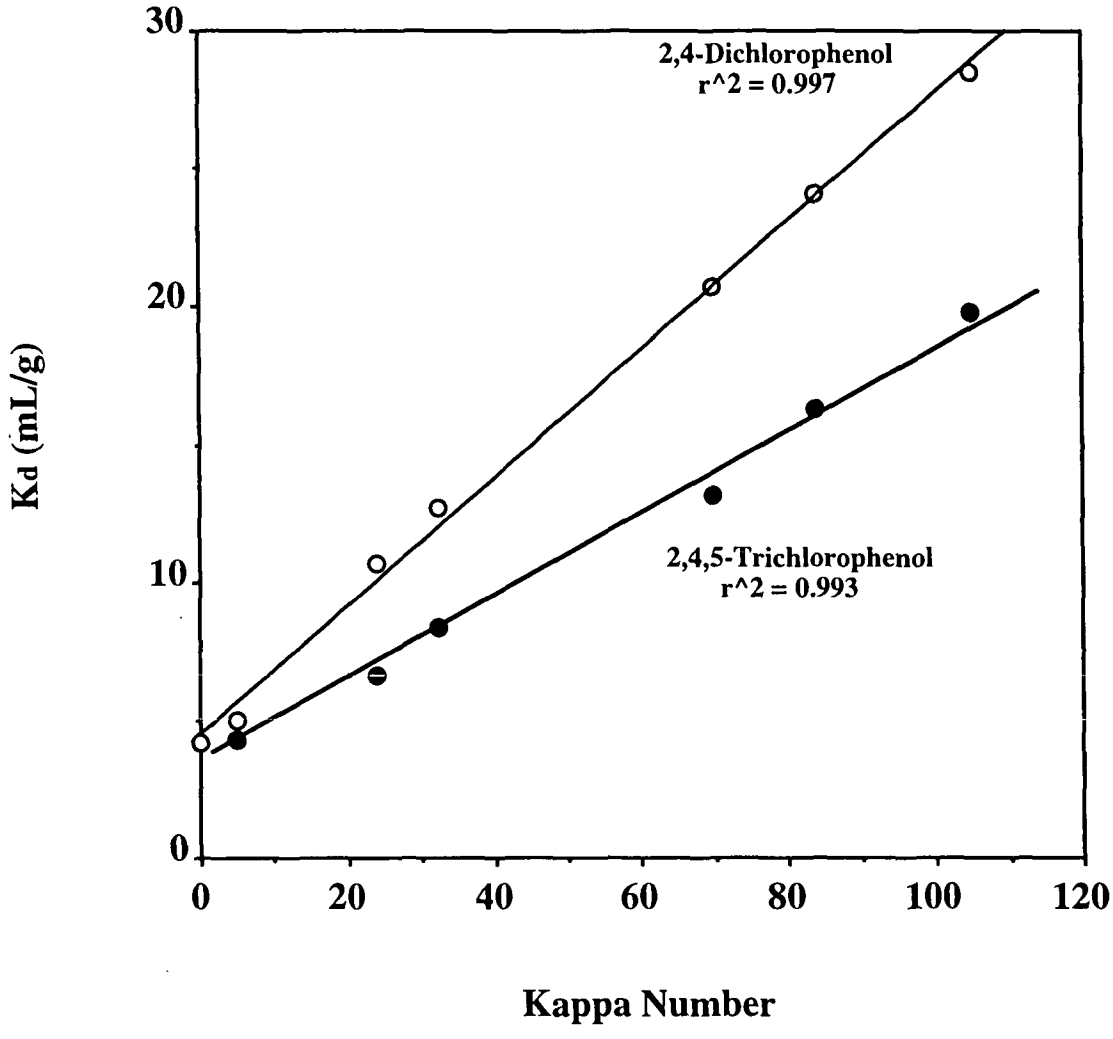


Figure 31. Fiber-water distribution coefficients for 2,4-dichlorophenol and 2,4,5-trichlorophenol versus the kappa number of the softwood fiber sorbents at pH of 8.00.

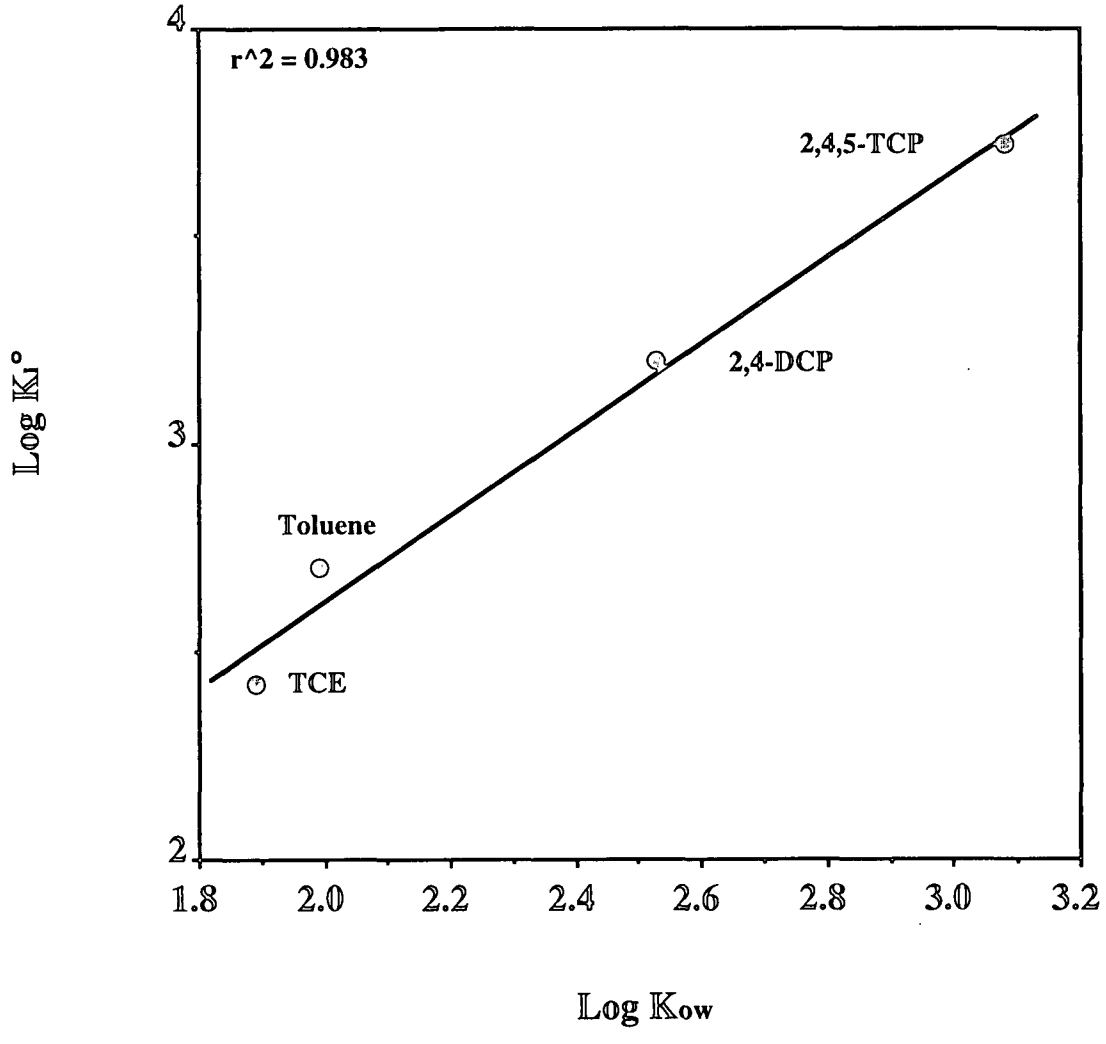


Figure 32. Relationship between $\log K_i^0$ and $\log K_{ow}$ values (data for toluene and TCE are from Ref. 69).

CONCLUSIONS

The results of this chapter demonstrate three important points on the retention of chlorophenols to fibrous solids: the ionized solutes do not sorb to pulp fibers, as demonstrated by accurate predictions of retention based on the compound's neutral form alone; lignin dominates the sorption process, which allows the sorption to the fiber's cellulose region to be neglected; and the lignin-water distribution coefficient can be predicted accurately by a linear free-energy relationship between $\log K_l^0$ and $\log K_{ow}$. These results provide a framework for understanding the behavior of organic bleaching residuals in a pulp and paper mill and also clarify the role of lignin containing materials such as lignin precipitates, fibers and shives.

THE EFFECT OF COSOLUTES, TEMPERATURE, AND INORGANIC SALTS ON SORPTION

INTRODUCTION

Understanding the effects on sorption of variables such as organic cosolutes, inorganic salts, and temperature is important in assessing and predicting the retention of hydrophobic organics by fibers. It was previously shown that the retention of chlorophenols to wood fibers and fiber-derived solids is controlled by their sorption to the fiber's lignin fraction and that the lignin-water distribution, K_l^0, could be estimated by a chemical's octanol-water distribution coefficient, K_{ow}. The mechanism involved in the sorption of nonpolar organics by other natural solids such as soils or sediments is thought to be similar to the distribution or partitioning of a compound between water and an organic solvent. For pulped wood fibers, the results of solid-water distribution coefficient measurements on both lignin and cellulose indicate that fibers and soil or sediment materials are quite similar from a sorption standpoint. For both sorbents, the retention of aqueous organic solutes is isolated largely to a hydrophobic polymer region that comprises a small fraction of the material's overall mass.[20,27,30,31] For pulped fibers, this phase is lignin which is mostly removed during pulping and bleaching. As with the organic fraction of soils and sediments, lignin is relatively hydrophobic. Thus, it may provide nonaqueous regions which solutes can associate with to escape the water phase (note: K_{om}^0 values measured[49] for the neutral forms of 2,4-DCP and 2,4,5-TCP are about 272 and 1165 mL/g, respectively, which are very close to their K_l^0 values of 340 and 1200 mL/g, respectively). Earlier results demonstrate that neither their ability to hydrogen bond with cellulose nor their ionization enhances chlorophenols retention to pulp fibers; sorption appears to

be due solely to the hydrophobic sorption of the neutral form of the chlorophenol compounds. As with the sorption of nonionic organics by soils and sediments, these results indicate that the key to modeling sorption lies in the water-solute interactions.

Correlations between log K_d and log K_{ow} indicate that sorption behavior can be predicted from a solute's aqueous activity coefficient.[33,34,48,49,91] But in the case of chlorophenols, predicting the effect of ionic strength is more difficult due to the presence of a large chlorophenolate population. Studies of chlorophenol sorption to organic sorbents under alkaline conditions indicate that the partitioning of chlorophenolates ion-paired with inorganic cations tends to dominate the sorption process. The evidence for this mechanism comes from studies of the octanol-water distribution of chlorophenols which indicate the strong presence of ion-paired chlorophenolates in the octanol phase,[75,76] and from increases in the solid-water distribution of chlorophenols at high pH levels due to increased ionic strengths.[49,78] Although these results do point to the participation of inorganic ions in the distribution of the ionized chlorophenols, other mechanisms are possible. At relatively high inorganic salt concentrations, the "salting out" of organic solutes can strongly increase their sorption. This occurs when inorganic ions compete for a solute's hydrating water and can affect neutral organics as well as hydrophobic ions.

Another variable that might affect the sorption of chlorophenols to pulp fibers is the presence of cosolutes. Bleaching filtrates in a kraft paper mill contain a rich variety of organic chemicals, but the concentration of any specific chemical is low. Thus, the aqueous phase of the effluents can be considered as a dilute solution containing numerous cosolutes. Given their low concentration, cosolute effects are expected to be minimal, but it is possible they will impact the process as cosorbates. This effect

is difficult to predict without a mechanistic model of the sorption process, but it does appear in some cases that low levels of cosolutes acting as cosorbates can significantly drop the distribution of a nonpolar organic to solids.[60]

THEORY

The fiber-water distribution coefficient for chlorophenols is controlled by the lignin-water distribution coefficient of the neutral form of the compound, K_l^0. It was previously shown that a chlorophenol's log K_l^0 correlates with its log K_{ow}. This result, along with the linear isotherms measured over a concentration region of 1 ppb to 1 ppm, indicates that the sorption may be more similar to a phase transfer process rather than to a specific interaction. Treating it as such allows K_l^0 to be rewritten in terms of the neutral solute's activity coefficients in the water (γ_w) and lignin (γ_l) phases,

$$K_l^0 = \frac{\gamma_w}{\gamma_l} \frac{\overline{V}_w}{\overline{V}_l \, \rho_l} \tag{44}$$

where C_s and C_w are the concentration of solute in the solid and water phases, respectively, and $\overline{V}_w$, $\overline{V}_l$, and ρ_l are the molar volume of the aqueous phase and the molar volume and density of the lignin phase, respectively. The volume and density terms were necessary to convert from mole fraction concentrations into units common for measured distribution coefficients. If lignin is an accommodating phase to the chlorophenols, which would be expected based on similarities to their structures, activity coefficients for these solutes in lignin are likely to be close to unity. It is also likely that changes in the molar volume and density of both the aqueous and lignin

phases associated with temperature and ionic strength changes in bleaching effluents and enviromental systems are small and can be neglected. This leaves the solute's activity in the water as the only variable and allows Eq. 44 to be rewritten as

$$K_l^0 = \beta \gamma_w \tag{45}$$

where β is a constant.

Temperature

The aqueous activity coefficient of a solute is related to temperature by[92]

$$\ln \gamma_w = \frac{\triangle H_s^E}{RT} + constant \tag{46}$$

Earlier, it was shown that at a given pH value, the fiber-water distribution coefficient could be expressed as (Eq. 42)

$$K_d \approx \alpha f_l K_l^0$$

The substitution of Eqs. 42 and 45 into 46 results in

$$\ln K_d = \frac{-\triangle H_{sorp}}{RT} + constant' \tag{47}$$

It should be noted that $\triangle H_s^E$ is the heat of aqueous dissolution for the organic solute (the transfer into water) while $\triangle H_{sorp}$ is the heat of sorption (the transfer out of water). This accounts for the sign change on the enthalpy term.

Inorganic Salts

The relation between a solute's aqueous phase activity coefficient at elevated inorganic salt concentrations (γ_w^{salt}) and the molar concentration of the salt is given by the well-known Setschenow equation[93,94]

$$\gamma_w^{salt} = \gamma_w \, 10^{K^s[salt]} \tag{48}$$

Here, γ_w is the distilled water or low salt level aqueous activity coefficient and K^s is the Setschenow constant for an inorganic salt and organic solute pair. The substitution of Eqs. 45 into 48 with some minor rearrangements produces a linear form

$$\log \, K_d^{salt} = \log \, K_d + K^s[salt] \tag{49}$$

Thus, plots of log K_d versus the molar concentration of the inorganic salt should result in a linear plot with its slope equal to the solute's Setschenow constant.

RESULTS AND DISCUSSION

Isotherm Measures

Figure 33 shows the linear fits of the sorption isotherms for the fiber-water distribution of 2,4,5-TCP to various kappa number pulps. The results indicate that a linear model of sorption can be used quite accurately in the concentration region relevant in bleaching effluents. But it is interesting to note that, over a much broader range, the isotherms do indicate a nonlinear trend. This is demonstrated by measuring the isotherm slopes in two different concentration regions (Table 5). The first region ranges from about 1 ppb to 500 ppb; the second is for solute concentrations above 1 ppm. As is shown, sorption is slowly decreasing. Attempts to fit this reduction, for example, with the traditionally used Freundlich model, were unsuccessful. From a mechanistic standpoint, this slight decrease may indicate that the fiber-water distribution of organic solutes is a complex process which cannot be placed neatly into an adsorption or absorption category.

Table 5. The slope of linear isotherms in two solute concentration regions.

	K_d (mL/g)	
	1 ppb $\sim$ 500 ppb	$\geq$ 1 ppm*
2,4-dichlorophenol	40.1	37.5
2,4,5-trichlorophenol	60.4	27.8

* the maximum concentrations of 2,4-dichlorophenol and 2,4,5-trichlorophenol were 6 and 500 ppm respectively.

To determine if surface area plays a role in the sorption process, pulp fibers were mechanically ground into powder and used as sorbents in distribution measurements. Table 6 shows a comparison of the solid-water distribution coefficients for the sorption of model compounds to both the ground and unground pulp fibers. The results demonstrate that the increased surface area has no effect on sorption. Experiments were also run to determine if the presence of other chlorophenols would change the shape of the measured isotherms (e.g., through competitive sorption). Figure 34 plots the isotherm of 2,4,5-TCP for the sorption to kappa number 69.8 softwood fibers using a series of chlorophenols as cosolutes including a five chlorophenol mixture (2-chlorophenol; 2,6-dichlorophenol; 2,4,6-trichlorophenol; 2,3,4,5-tetrachlorophenol; and pentachlorophenol). These results and similar results for 2,4-dichlorophenol (Fig. 35) again show no effect.

Table 6. The sorption of 2,4-dichlorophenol and 2,4,5-trichlorophenol to ground and unground kappa number 69.8 softwood fibers at pH of 7.00.

	K_d (mL/g)	
	unground pulp	ground pulp
2,4-dichlorophenol	46.4 ± 0.723	46.4 ± 1.01
2,4,5-trichlorophenol	65.9 ± 1.07	64.3 ± 1.75

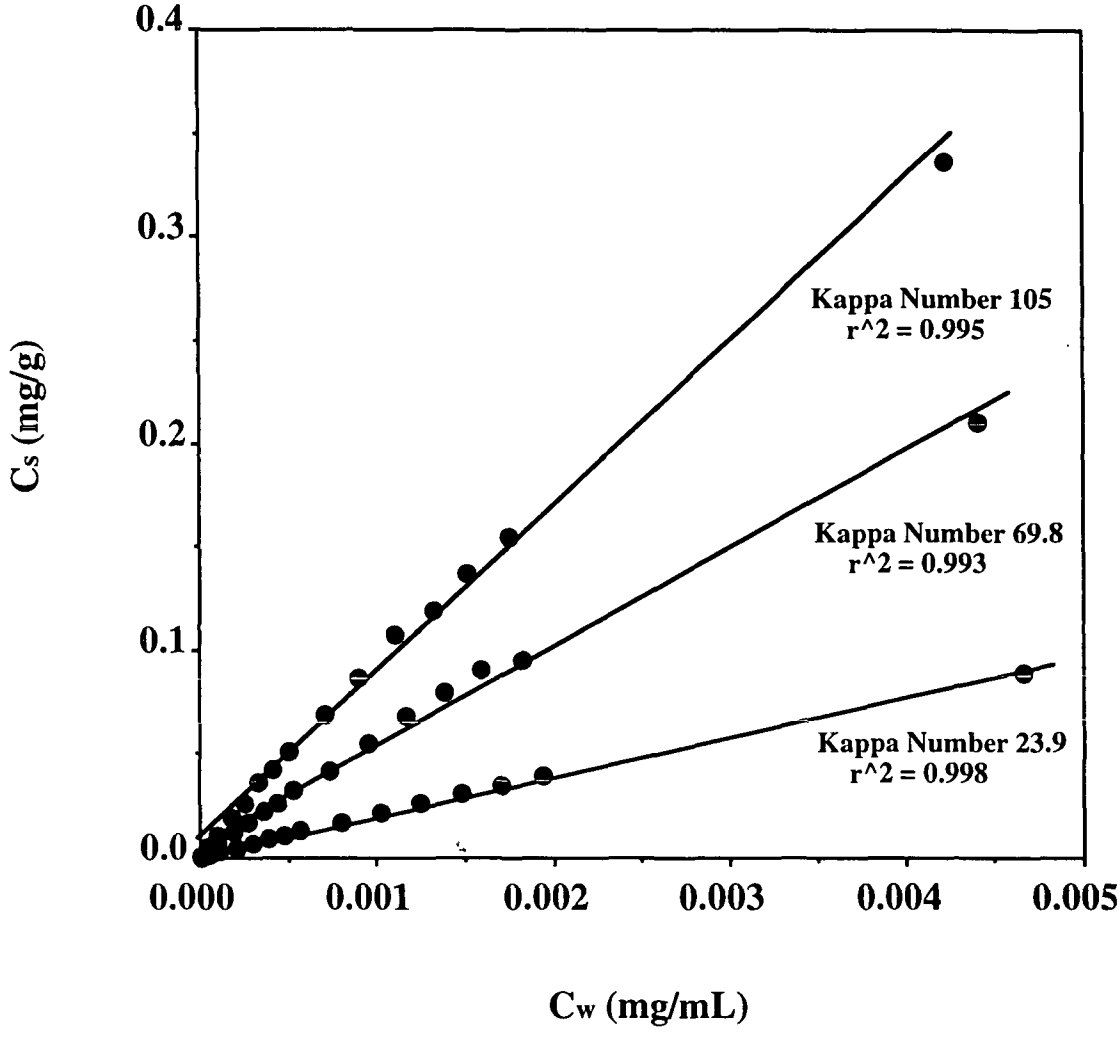


Figure 33. Isotherms for the sorption of 2,4,5-trichlorophenol to various kappa number softwood fibers at 25°C and pH of 7.00.

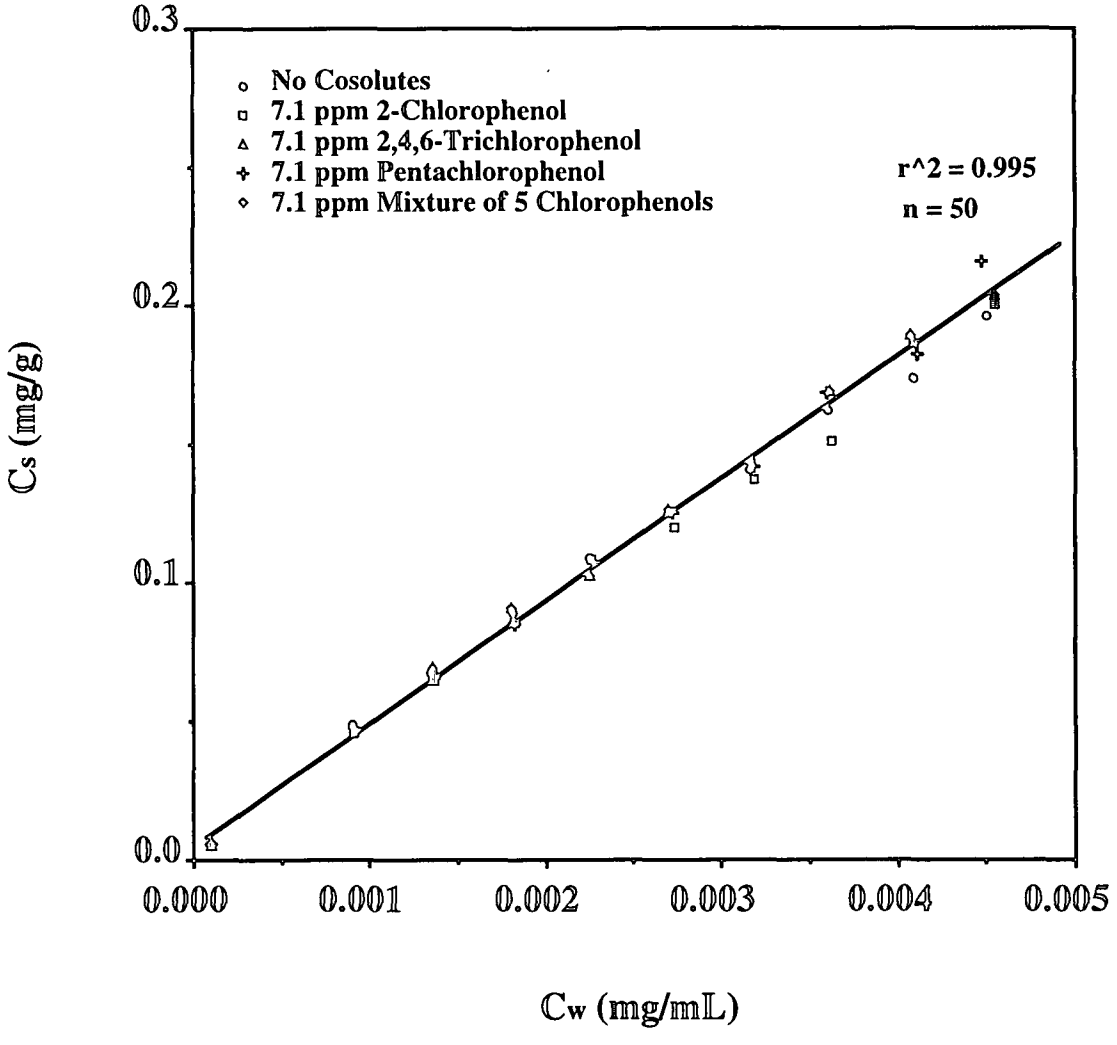


Figure 34. Competitive isotherms for the sorption of 2,4,5-trichlorophenol to kappa number 69.8 softwood fibers.

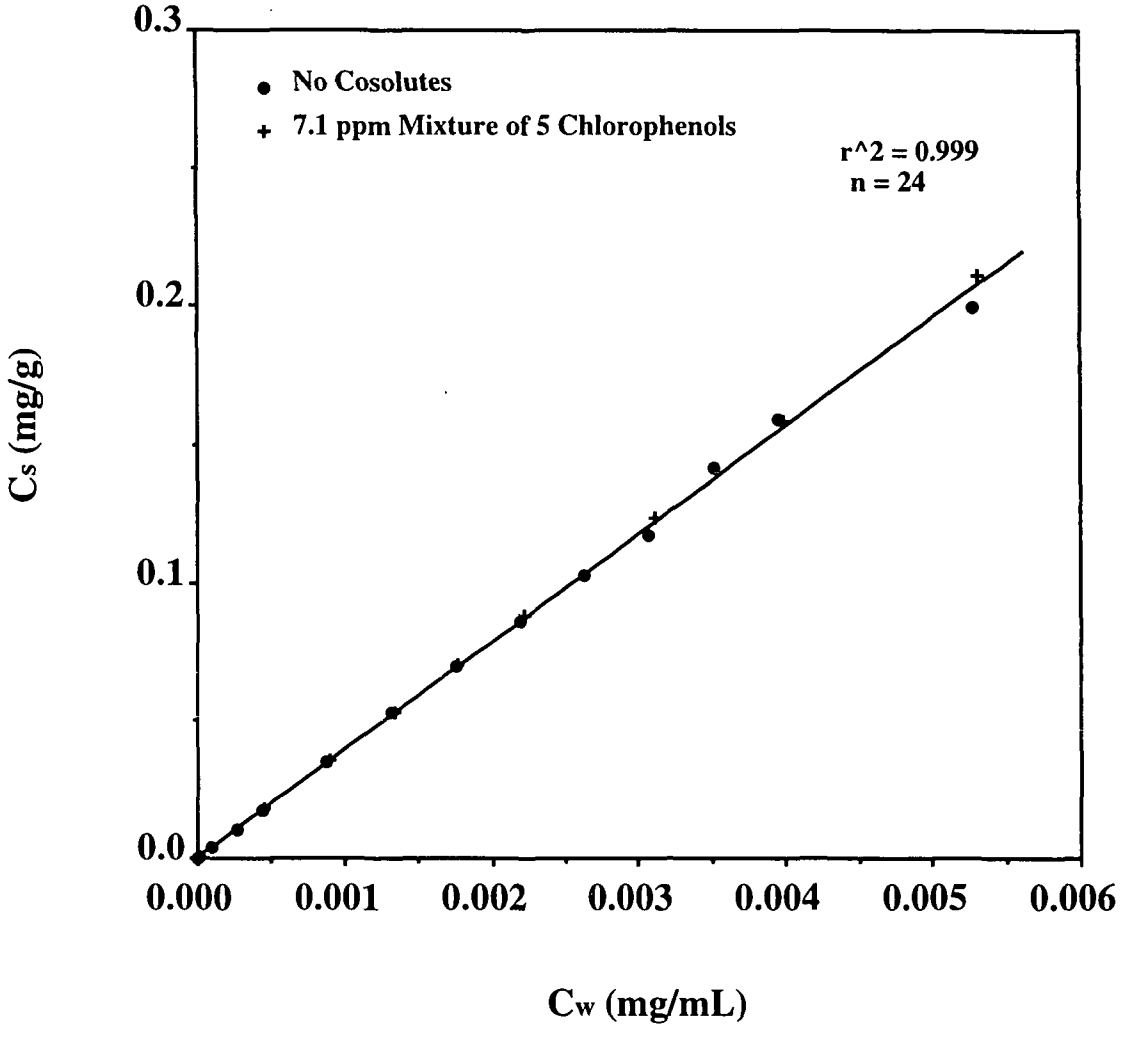


Figure 35. Competitive isotherms for the sorption of 2,4-dichlorophenol to kappa number 69.8 softwood fibers.

Temperature Effects

Figure 36 plots the natural log of the measured distribution coefficients as a function of the inverse of absolute temperature in accordance with Eq. 47. The data covers the temperature region that is of environmental interest (5 - 100°F) and appears to show strong linear correlations. The estimates for the heats of sorption from the slopes of these lines are -1.83 and -2.55 Kcal/mol for 2,4-DCP and 2,4,5-TCP, respectively. Given the measured and estimated heats of aqueous dissolution for benzene (0.50 Kcal/mol), phenol (1.7 Kcal/mol), and pentachlorophenol (3.92 Kcal/mol) at 25°C,[95–99] it appears these values are consistent with the enthalpy change associated with aqueous dissolution. Thus, temperature effects should be predictable from solubility information, but the results also indicate that K_d has only a weak temperature dependency. For 2,4,5-TCP, measurements indicate about a 4% drop in K_d for every 5°C temperature increase. For a 20°C increase which might be associated, for example, with a seasonal change, the distribution coefficient would drop by only 16%. This weak temperature dependency can be augmented or offset by the temperature dependency of an organic acid's pK_a value. A chlorophenol's pK_a may decrease or increase with temperature, the extent of which is dependent on the specific phenol, but shifts are usually in the range of 0.01 to 0.03 pK_a units per each degree rise in absolute temperature.[61] Thus, for organic acids, estimates of temperature effects must take into account the temperature dependency of the compound's pK_a value.

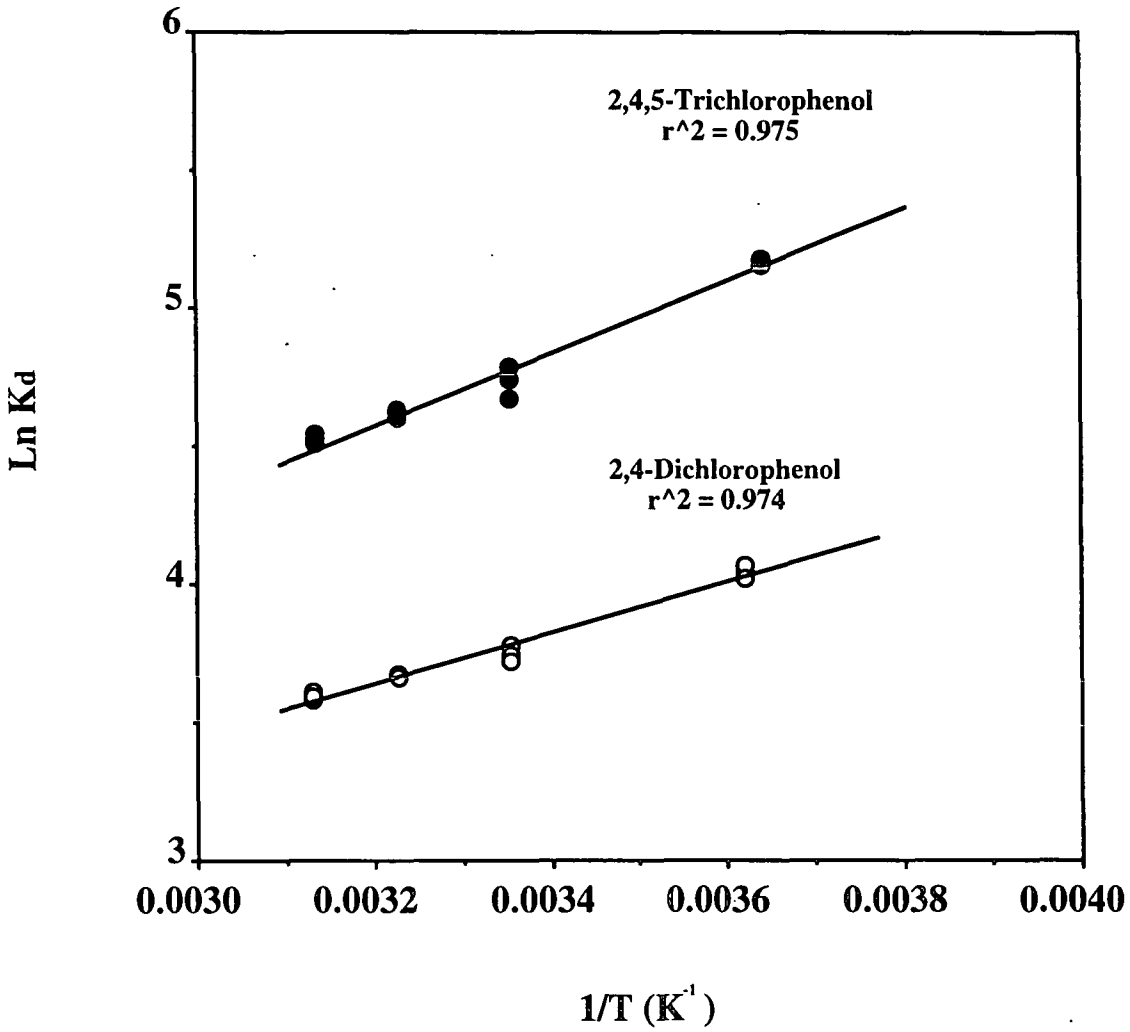


Figure 36. Temperature dependency plots for the sorption of 2,4-dichlorophenol and 2,4,5-trichlorophenol to kappa number 69.8 softwood fibers at pH of 4.00.

Inorganic Salt Effects

Figure 37 plots K_d as a function of pH for the sorption of 2,4,5-TCP to kappa number 69.8 softwood fibers at two different inorganic salt levels. The plot demonstrates the importance of the salting-out mechanism with the use of potassium chloride. At the lower pH values where the trichlorophenol is completely in its neutral form, the presence of salt causes a strong increase in the sorption. At high pH levels where the trichlorophenol is completely ionized, sorption is eliminated under both high and low salting conditions. These results are consistent with a salting-out mechanism, while the lack of sorption at high pH levels is inconsistent with ion pairing. Further evidence for the salting-out mechanism comes from plots of K_d vs. the fraction of the compound in its neutral form. From previous measurements on this system, it was found that sorption is isolated to the neutral form of the chlorophenol compounds. As demonstrated in Figs. 38-41, the sorption for 2,4-DCP and 2,4,5-TCP at both low ionic strength and at high KCl concentrations start out at the same point when the compound is completely in its ionized form (i.e., no sorption). But, as the population of the neutral molecules increases, the two lines diverge with the sorption under high inorganic salt concentrations having the higher slope. This indicates that the salting-out of neutral compounds, rather than the participation of the chlorophenolate species, causes the increased sorption.

Plots of log K_d for the sorption of 2,4-DCP and 2,4,5-TCP against the molar concentration of KCl are shown in Figs. 42 and 43. As expected on the basis of the salting out mechanism (Eq. 49), the plots are linear. The fits for the dichlorophenol sorption are somewhat less accurate, especially at the lower kappa numbers. This is caused by attempts to measure changes which are close to the variation in the

sorption measurement. The slopes of these lines give KCl Setschenow constants of 0.14 and 0.22 for di- (using the fit for kappa number 105 only) and trichlorophenol, respectively. These estimates are consistent with salting constants for other salts and organic solutes, which range from about 0.1 to 0.4.[100–103] For the distribution of chlorophenolics in bleaching effluents, these results indicate that the effect of inorganic salts will be small. For most paper mills, the concentration of ions in effluent streams will typically be in the 100-ppm range ($\sim$ 0.001 M). At these levels, the predicted salting effects are negligible. But as the industry moves towards greater mill closure, these concentrations as well as the salting-out effect are expected to climb. It should be noted that KCl was the only salt tested here. The choice of KCl was somewhat arbitrary, but consideration was given to the fact that past sorption studies had attributed increased sorption of chlorophenol chemicals by sediments to an ion-pairing mechanism with potassium (using a KCl solution).

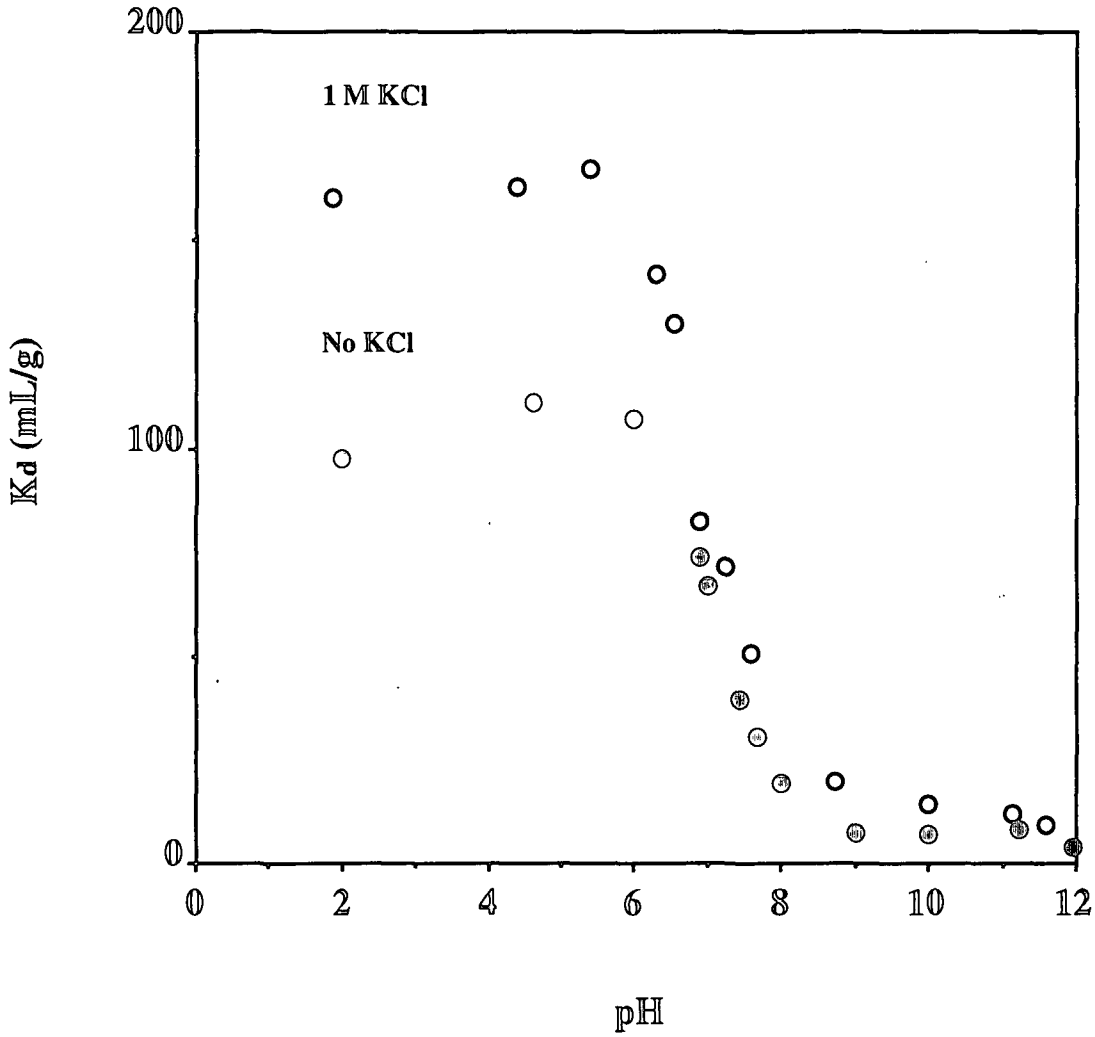


Figure 37. The sorption of 2,4,5-trichlorophenol to kappa number 69.8 softwood fibers with no salt and 1 M KCl concentrations.

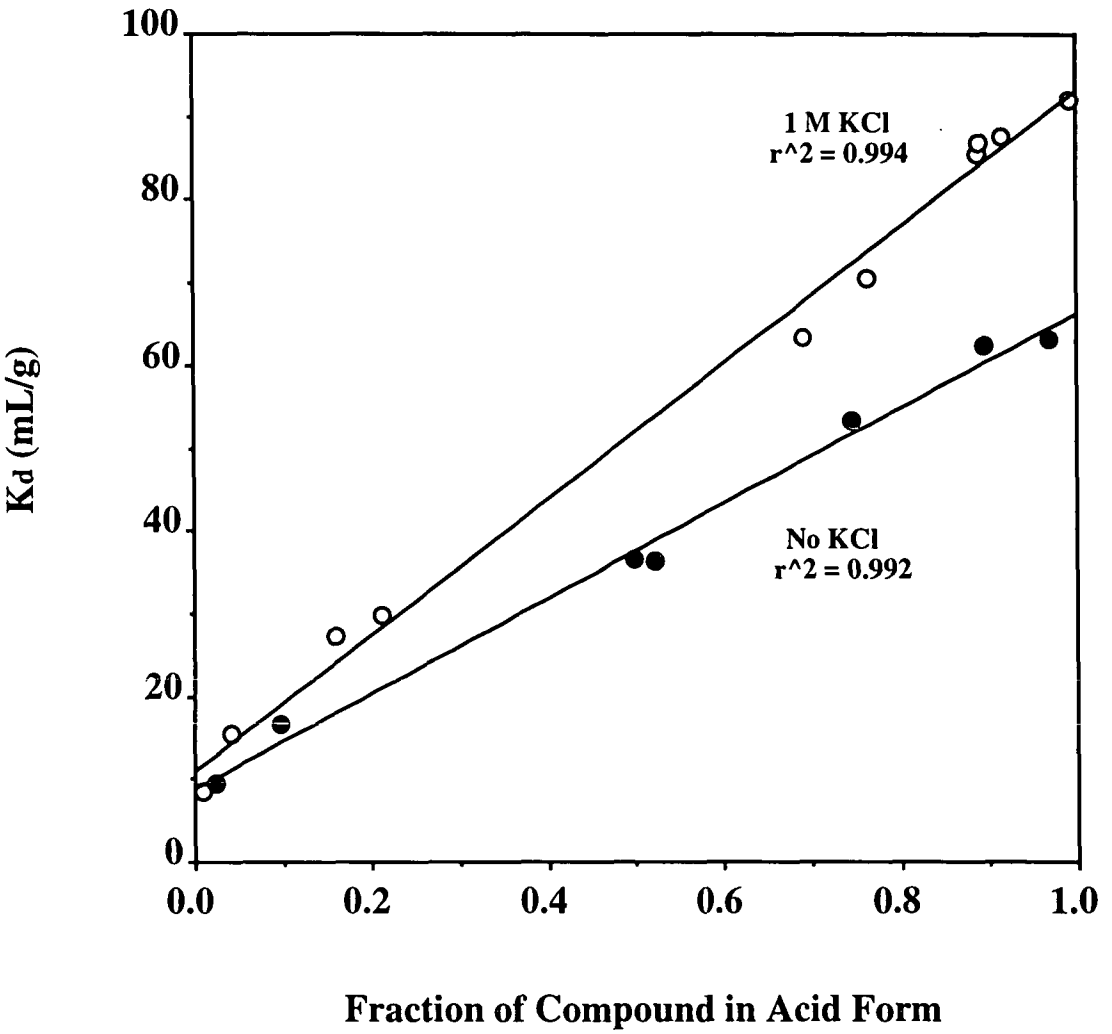


Figure 38. The sorption of 2,4-dichlorophenol to kappa number 105 softwood fibers as a function of the chlorophenol fraction in its acid form with no salt and 1 M KCl concentrations.

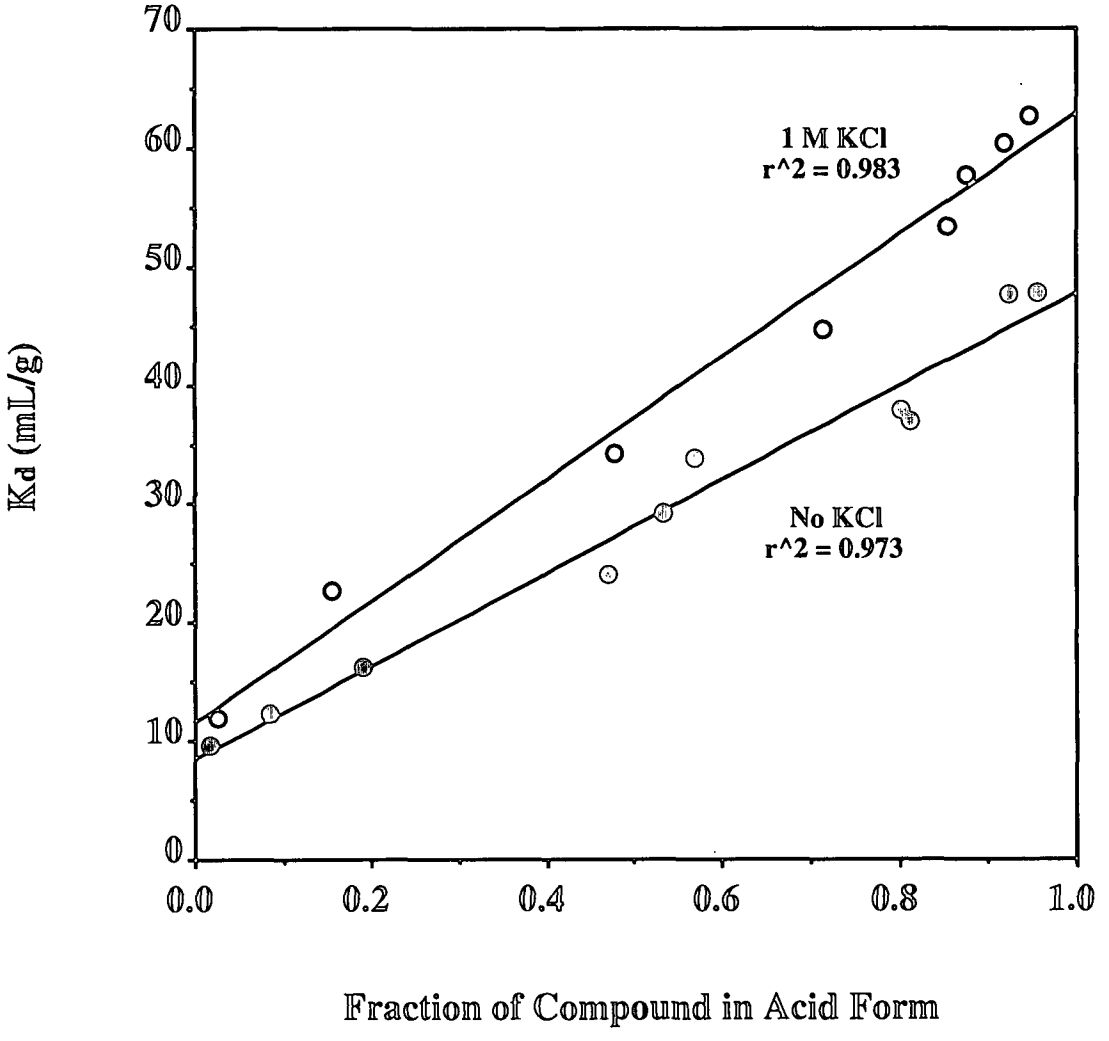


Figure 39. The sorption of 2,4-dichlorophenol to kappa number 69.8 softwood fibers as a function of the chlorophenol fraction in its acid form with no salt and 1 M KCl concentrations.

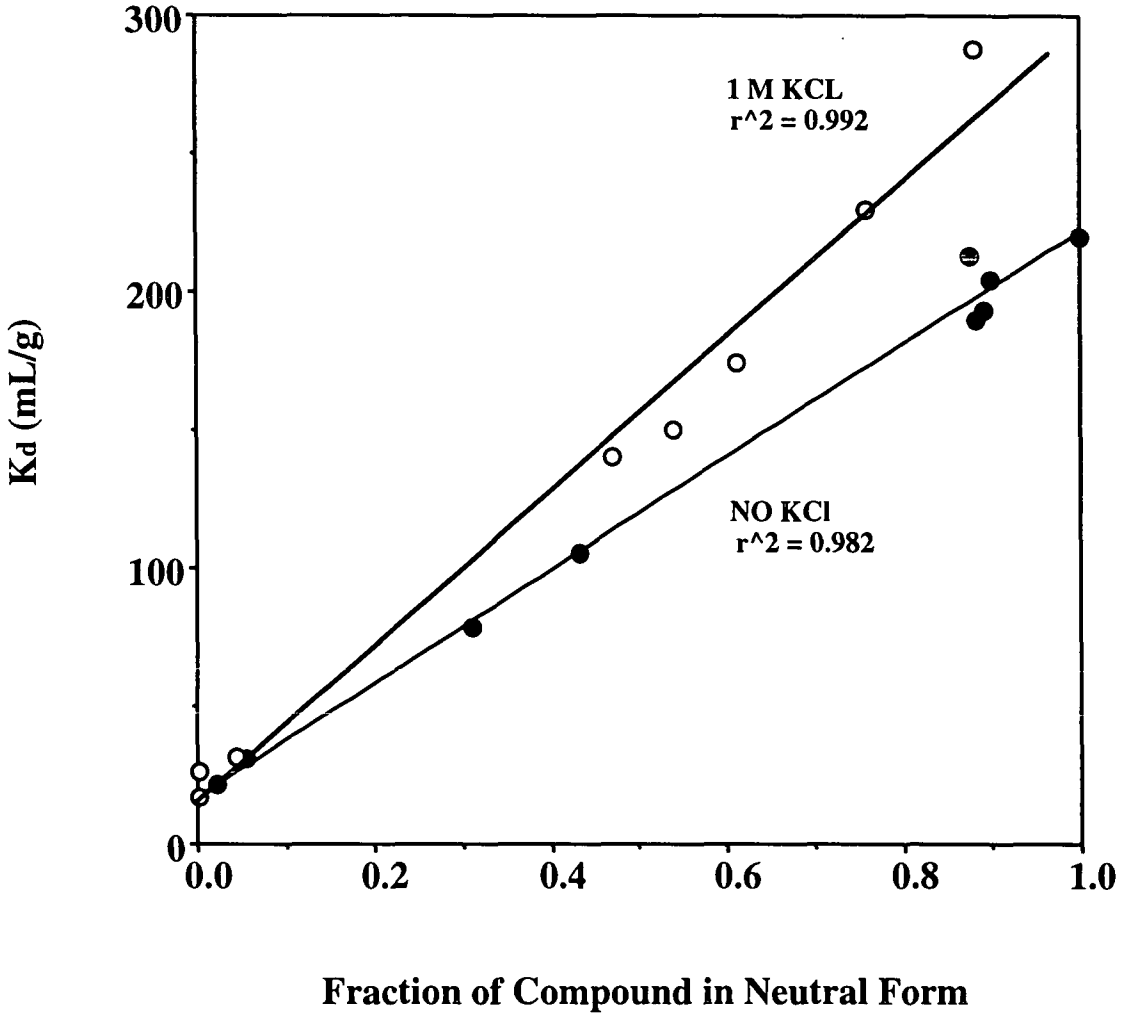


Figure 40. The sorption of 2,4,5-trichlorophenol to kappa number 105 softwood fibers as a function of the chlorophenol fraction in its acid form with no salt and 1 M KCl concentrations.

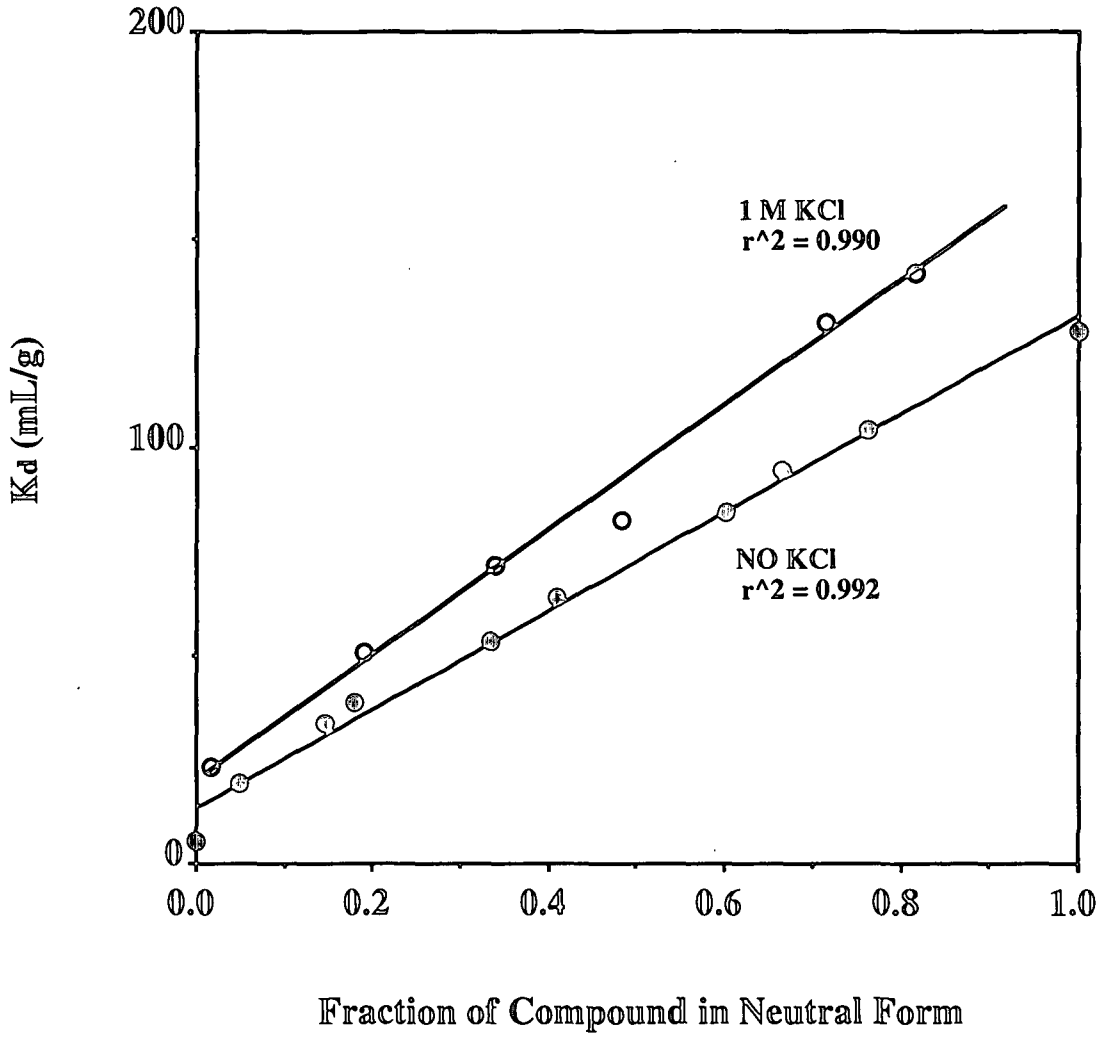


Figure 41. The sorption of 2,4,5-trichlorophenol to kappa number 69.8 softwood fibers as a function of the chlorophenol fraction in its acid form with no salt and 1 M KCl concentrations.

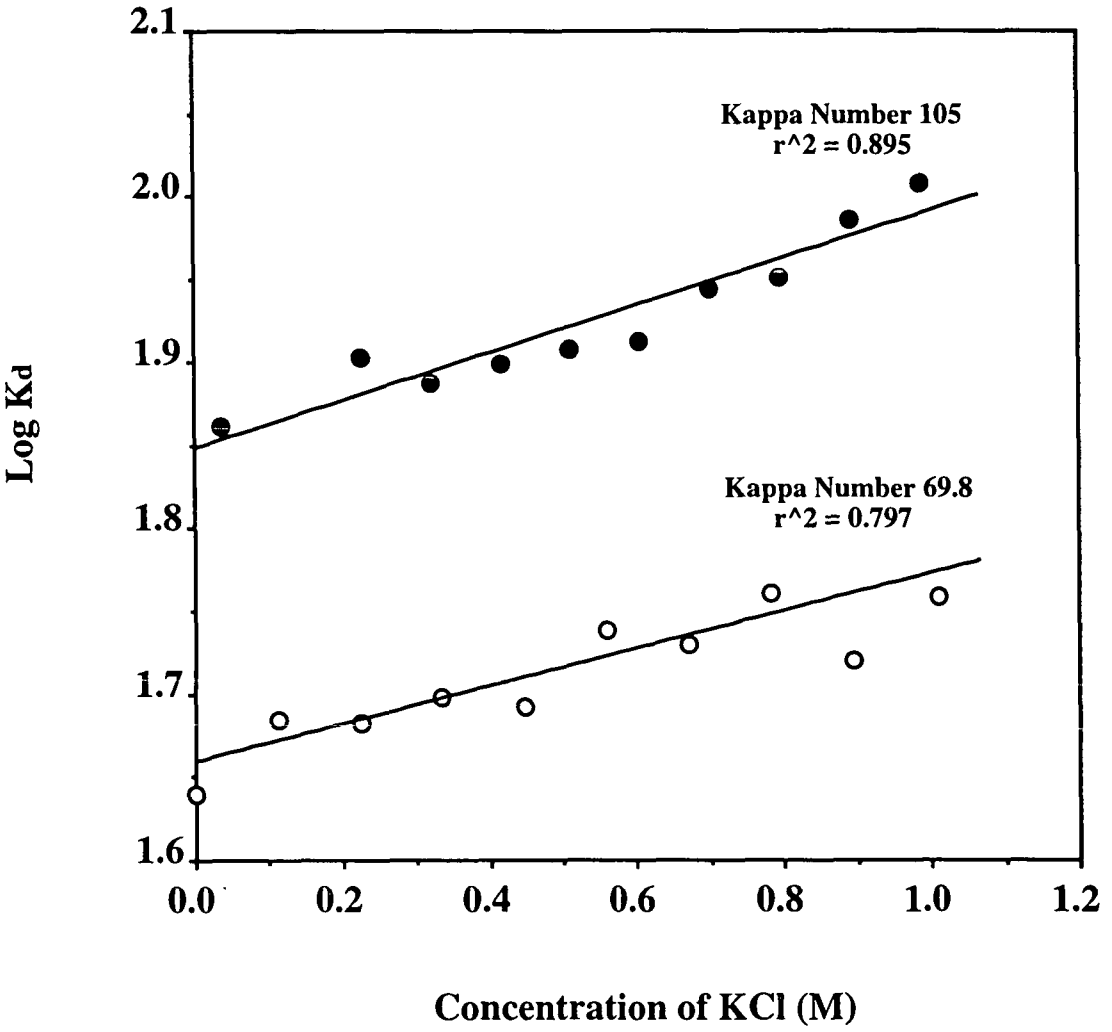


Figure 42. The sorption of 2,4-dichlorophenol to kappa numbers 69.8 and 105 softwood fibers as a function of KCl concentration.

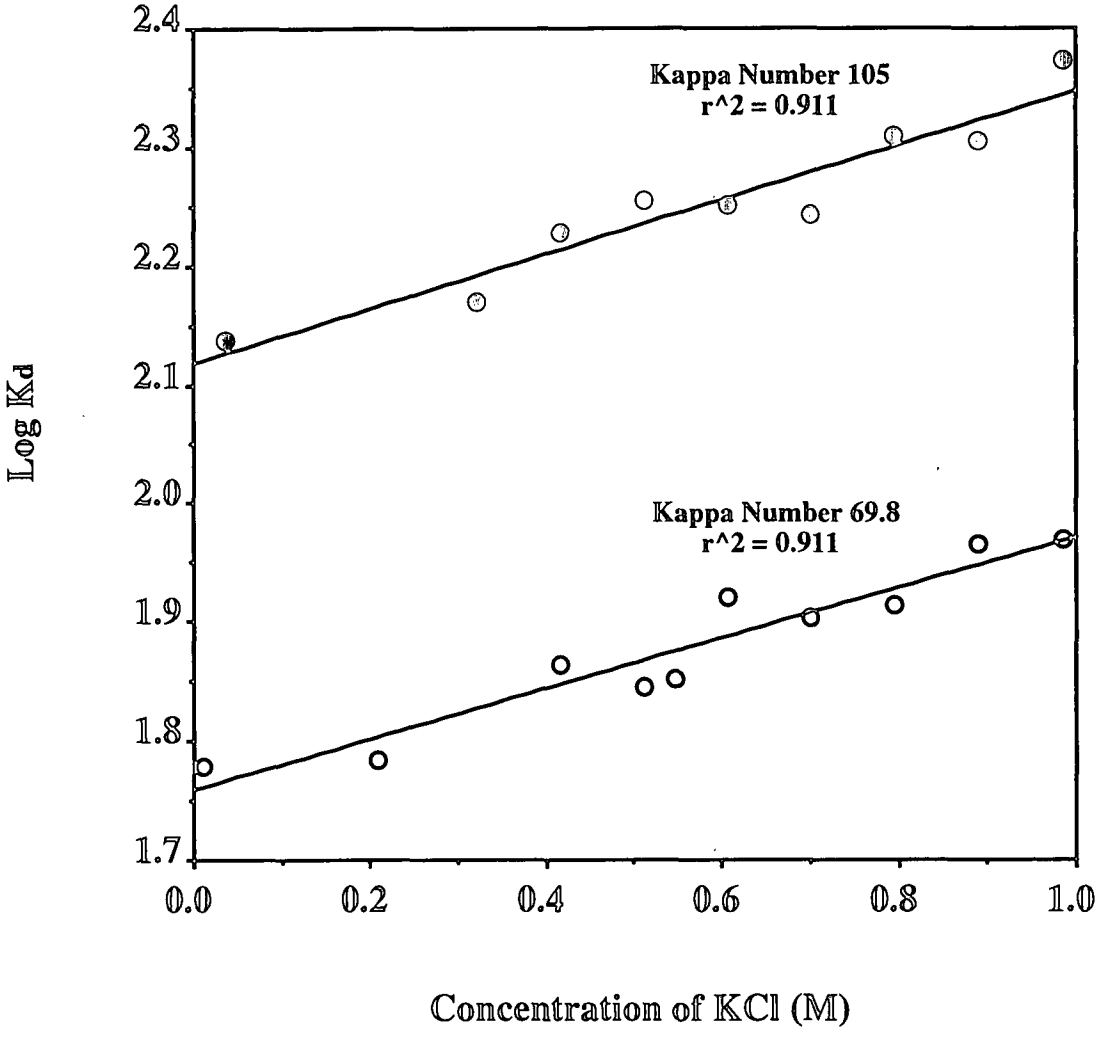


Figure 43. The sorption of 2,4,5-trichlorophenol to kappa numbers 69.8 and 105 softwood fibers as a function of KCl concentration.

CONCLUSIONS

The results of the experiments outlined here indicate the fiber-water distribution of chlorophenols can be treated accurately as a phase distribution process. Isotherms demonstrate no dependency on solute or cosolute levels, and the lack of change in distribution coefficients at increased fiber surface areas implies the fiber derived materials in bleaching effluents such as fines and precipitates can be treated on a mass basis. Similarities with a phase transfer were further promoted by the successful treatment of temperature and inorganic salt effects on fiber-water distribution coefficients based on the impact of these variables on the chlorophenol's aqueous activity coefficient. Although a phase equilibrium treatment was very successful in this case, it should be noted that no direct evidence of this mechanism was presented. The question of adsorption vs. absorption typically sparks heated debate.[33] Most of the evidence presented on either side pertains to isotherm data which is typically unreliable in identifying retention mechanisms. It appears the hydrophobic water-solid transfer of an organic solute which plays a role in many systems is poorly understood, but, for this project, the treatment of the process as a phase equilibrium problem was very effective.

THE EFFECT OF SUBSTRATE CONCENTRATION ON SORPTION

INTRODUCTION

A perplexing phenomenon with important implications in the study of sorption in environmental systems is the apparent reduction in sorption with increasing sorbent levels in experimental batch studies.[21,48,83–89] The low sorbate levels used in measuring solute distributions for environmental studies should produce a constant activity coefficient in the aqueous phase (i.e., infinitely dilute). Thus, the phenomenon, commonly referred to as the "solids effect," is an apparent contradiction to thermodynamic laws. Two principal schools of thought exist on the solids effect. The first hypothesizes that submicron colloidal material concentrations (commonly referred to as the "third phase") increase proportionately with the solids concentration. This material may be an effective sorbent of organic chemicals but may not be separable from the aqueous phase for distribution coefficient measurements. This would cause a steady decease in K_d values with increasing solids or sorbent concentrations. The second dominant theory ties decreased sorption to the increased particle interactions that will occur at higher solids levels. The greater frequency of particle-particle collisions may cause collision-induced desorption that counters retention.

The material that is the basis of the third-phase argument includes microparticles or macromolecules in the diameter range from about a nanometer to a micrometer. These materials are too small to settle out of an aqueous solution and travel throughout the phase primarily by Brownian motion. The mechanism involved in the lowering of a distribution coefficient by the third phase supposes that colloidal material offers organic solutes a region into which they can partition to escape the

aqueous phase.[21,86,87,104–106] Evidence for this can be found in increased solubilities of organic solutes with increasing colloidal levels[66,107–109] and in experiments where dialysis bags are used to separate colloids from an aqueous solution, showing that the chemicals are preferentially retained with the colloids.[110,111] The retention mechanism for the third phase appears to be similar to that for larger solid sorbents. Just as the polarity of a solid substrate and the aqueous activity coefficient of a solute are shown to affect solid-water distributions, experiments which claim to measure the retention of organic solutes by colloidal materials indicate that sorption is dependent on both colloid and solute hydrophobicity.[112–113] It has also been estimated that a colloid material's distribution coefficient is similar to the distribution coefficient for the sorbent which it is derived from.[114]

There is ample evidence that third-phase arguments apply to many situations where sorption is lower than expected,[115] but experiments designed to factor out third-phase materials (involving the use of model sorbents) have demonstrated that the third-phase retention mechanism cannot completely account for decreased sorption in all cases.[116] This has led to the development of alternative theories for the solids effect. The most popular are particle interaction models which credit the lowering of equilibrium sorption with an increase in sorbent-sorbent interactions which accompany increased solids levels. The most compelling of these is the model proposed by DiToro that credits the lowering of sorption to a collision-induced desorption step in which a fraction of previously sorbed solutes are freed.[84,116] The basic assumption is that the energy from a collision is sufficient to break the weak bonds that are responsible for the retention of a solute to a solid surface. Although this model is appealing in its qualitative form, attempts to develop a mechanistic model have been

unsuccessful. In this chapter, a model for collisional induced desorption is presented and discussed.[85] Equations are also developed to test the third-phase sorption hypothesis. These results are then discussed in the context of experiments of third-phase and solid concentration effects on the sorption of model organic chemicals to pulped wood fibers.

THEORY

Collisional Desorption Model

Model Development

Environmental transport of suspended particles in water occurs principally through Brownian diffusion.[117] When two particles collide, all or part of their kinetic energy is deposited at the particle surface. Einstein has shown that the particles involved have surprisingly high mean velocities through Brownian motion; for instance, the mean velocity of a 2.5-fg platinum particle in water at 19°C is 8.6 cm/s.[118] The mean displacement, however, is smaller by four orders of magnitude, since the motion of the particle is random. On the basis of simple collision theory,[119] the disparity between displacement and velocity requires that the two particles collide extensively through translational Brownian motion before they fully separate. Rotational Brownian motion further increases the collision frequency if the particles are nonspherical. For nonsuspended particles, the collisions are induced through mixing. The more turbulent the mixing, the more frequent and energetic the collisions.

The energy transferred to the surface will be dissipated at the surface[120] and is

essentially equivalent to heat. Collision of the two platinum particles of the type described above will lead to a surface-temperature rise of a fraction of 1 K, depending on the depth of the surface impacted. Since the sorption coefficient is inversely proportional to temperature,[121] collision will lead to a spontaneous desorption of a small fraction of solute. If the collisions are infrequent, the displaced solute will simply resorb, and conventional partitioning behavior will result. However, if the collisional frequency is high enough, the conventional equilibrium concentrations will not be restored. In other words, a balance will be struck between the frequency of collision and the rate resorption.

Consider the equilibrium

$$S + P \underset{k_2}{\overset{k_1}{\rightleftharpoons}} SP$$

where S, P, and SP are solute, particle, and reversibly sorbed solute, respectively. It follows that

$$\frac{d[SP]}{dt} = k_1 [S] [P] - k_2 [SP] \tag{50}$$

The total amount of sorbed solute can be rewritten as

$$[SP] = [SP]_0 + [S]_0 - [S] \tag{51}$$

where the subscript zero indicates initial concentrations. The concentration of the solute in the aqueous phase can be written in terms of the total solute concentration ($[S]_T$) as

$$[S] \;=\; [S]_T \;-\; [SP] \tag{52}$$

These results along with the assumption that the amount of sorption sites is unlimited, $[P] \approx [P]_0$, allow Eq. 50 to be rewritten as

$$\frac{d[SP]}{dt} \;=\; k_1\,[P]_0\,[S]_T \;-\; k_1\,[P]_0\,[SP] \;-\; k_2\,[SP] \tag{53}$$

Defining $k' = k_1[P]_0 + k_2$ further reduces Eq. 53 to

$$\frac{d[SP]}{dt} \;=\; k_1\,[P]_0\,[S]_T \;-\; k'\,[SP] \tag{54}$$

For a general time period, t, this equation integrates to

$$[SP] \;=\; [SP]_0\,e^{-k't} \;+\; \left(\frac{k_1}{k'}\right)[P]_0\,[S]_T\,(1 \;-\; e^{-k't}) \tag{55}$$

At the moment of collision, the particle receives an energy pulse that desorbs a small fraction of solute. If the fraction remaining on the particle is designated as f, then multiplying the $[SP]$ term in Eq. 55 by f gives

$$[SP] = f[\,[SP]_0\, e^{-k't} + (\frac{k_1}{k'})\,[P]_0\,[S]_T\,(1 - e^{-k't})\,] \tag{56}$$

This is the amount of solute which remains sorbed to the particles after collision. If τ is defined as the period between collisions, [SP] just before the next collision will be given by substituting Eq. 56 for $[SP]_0$ into Eq. 55. Hence

$$[SP] = (\frac{k_1}{k'})\,[P]_0\,[S]_T\,(1 - e^{-k'\tau}) +$$

$$fe^{-k'\tau}\,[\,[SP]_0\, e^{-k'\tau} + (\frac{k_1}{k'})\,[P]_0\,[S]_T\,(1 - e^{-k'\tau})\,] \tag{57}$$

$$= (\frac{k_1}{k'})\,[P]_0\,[S]_T\,(1 - e^{-k'\tau}) +$$

$$f\, e^{-k'\tau}\,(\frac{k_1}{k'})\,[P]_0\,[S]_T\,(1 - e^{-k'\tau}) + f\,[SP]_0\, e^{-2k'\tau} \tag{58}$$

Just before the subsequent collision

$$[SP] = (\frac{k_1}{k'})\,[P]_0\,[S]_T\,(1 - e^{-k'\tau}) + f\, e^{-k'\tau}\,[P]_0\,[S]_T\,(1 - e^{-k'\tau}) +$$

$$f^2 e^{-2k'\tau}\,(\frac{k_1}{k'})\,[P]_0\,[S]_T\,(1 - e^{-k'\tau}) + f^2\,[SP]_0\, e^{-3k'\tau} \tag{59}$$

Equation 59 was obtained by multiplying Eq. 58 by f and substituting the result for the $[SP]_0$ term in Eq. 55 as before.

After n collisions

$$[SP] = \left(\frac{k_1}{k'}\right)[P]_0\,[S]_T\,(1 - e^{-k'\tau})\sum_{j=0}^{n}(f\,e^{-k'\tau})^j + f^n\,[SP]_0\,e^{-(n+1)k'\tau} \quad (60)$$

For large n, the summation $\sum_{j=0}^{n}(f\,e^{-k'\tau})^j$ converges to $1/(1 - fe^{-k'\tau})$, and the last term in Eq. 60 approaches zero. Hence

$$[SP] = \left(\frac{k_1}{k'}\right)[P]_0\,[S]_T\,\frac{(1 - e^{-k'\tau})}{(1 - f\,e^{-k'\tau})} \quad (61)$$

If $f = 1$, Eq. 61 reverts to the conventional sorption equation. As an order of magnitude illustration, if $k_1 = 1 \times 10^{-2}\text{min}^{-1}$ [118] and $\tau = 0.1$ min, then $[SP]$ decreases by half if f decreases from 1 (conventional) to 0.999. Thus, collision-induced desorption of 0.1% is sufficient to cause a sizable decrease in sorption under these conditions if, on the average, a collision occurs every 6 seconds. The collision frequency will depend upon the shape of the particles and diffusion-related parameters as well as the flow parameters (e.g., Reynold's number) if mixing is involved. The f term will be governed by the heat of sorption, surface effects related to vicinal water, the depth of the surface affected, particle size distribution, and other factors.

The (reversible) partition coefficient K can be written as

$$K = \frac{\frac{[SP]}{[P]_0}}{[S]_T - [SP]} \quad (62)$$

$$= \frac{k_1\,(1 - e^{-k'\tau})}{k'\,(1 - f\,e^{-k'\tau}) - k_1\,[P]_0\,(1 - e^{-k'\tau})} \quad (63)$$

The conventional (reversible) distribution coefficient (i.e., without the collision effect), K^0, is k_1/k_2. Equation 61 can be rearranged to

$$K = \frac{K^0 (1 - e^{-k'\tau})}{1 - f\, e^{-k'\tau} + K^0 [P]_0 (1 - f)\, e^{-k'\tau}} \tag{64}$$

Equation 64 is the general equation governing both particle-induced and conventional sorption. At low solids, the exponential term vanishes since τ is large and $K = K^0$. Thus, the difference in magnitude between conventional and collisional desorption is governed by τ, the interval between collisions.

A potential difficulty with the above scheme is that a collision of water molecules with the particle surface occurs much more often and with energies not much different than those involved in interparticle collision.[118] However, energy transfer in collisions between species of different sizes is much less efficient than those between similar size particles. For example, the fraction of kinetic energy transferred (f_{trans}) from one particle to the other in an elastic head-on collision is given by

$$f_{trans} = \frac{4\,\frac{m_1}{m_2}}{(1 + \frac{m_1}{m_2})^2} \tag{65}$$

where m_1 and m_2 are the masses of the two particles involved, with particle 2 being considered to be initially at rest on a relative basis.[122] For two particles of equal mass, i.e., $f_{trans} = 1$, all the kinetic energy is transferred. Hence, the energy transferred during particle-particle collision is several orders of magnitude greater than that involved in water-particle collision.

Model Discussion

DiToro's model for collisional desorption is based on the scheme

$$S + P \underset{k_2}{\overset{k_1}{\rightleftharpoons}} SP$$

$$SP + P \xrightarrow{k_3} S + 2P$$

from which

$$K = \frac{K^0}{1 + [P]_0 K^0 \frac{k_3}{k_1}} \tag{66}$$

Lande[123] has objected to the scheme on the grounds that an equilibrium cannot include an irreversible step. Thus, the basis of Eq. 64 is uncertain, but it applies quite well to the experimental data at an empirical level. Equations 62 and 64 predict similar dependencies of K on particle concentration. Equation 64 can be rearranged to

$$K = \frac{K^0}{\frac{1 - f\, e^{-k'\tau}}{1 - e^{-k'\tau}} + K^0 [P]_0 \frac{(1 - f)\, e^{-k'\tau}}{1 - e^{-k'\tau}}} \tag{67}$$

Since $k_1 > k_2$, then at high $[P]_0$, $k_1[P]_0 > k_2$ and $k'\tau \approx k_1[P]_0\tau$ (from Eq. 53). Since τ is inversely proportional to $[P]_0$, the exponential term will be independent of $[P]_0$.

Also, since f approaches 1, the term $(1 - fe^{-k'\tau})/(1 - e^{-k'\tau})$ will be only slightly greater than 1, and Eq. 64 and 66 will be similar in form.

DiToro[84,116] notes that the coefficient (k_3/k_1) in Eq. 64 tends to approximate 1. The equivalent term in Eq. 67 is $(1 - f)e^{-k'\tau}/(1 - e^{-k'\tau})$. Setting this term to 1 gives

$$f = 2 - e^{k'\tau} \tag{68}$$

Mackay and Powers[124] calculated that the interval between Brownian collisions corresponding to a particle density of 1.3×10^{11} particles/L is approximately 1 hour. However, this value applies only to the initial collision, and τ will be very much lower since multiple collisions will occur before the particles fully separate.

Finally, given DiToro's success in applying Eq. 64 to a large body of sorption data,[84] we recommend that the equation be retained with its constants redefined. If $(1 - fe^{-k'\tau})/(1 - e^{-k'\tau}) = 1$ in Eq. 67, then it simplifies to

$$K = \frac{K^0}{1 + K^0 [P]_0 C} \tag{69}$$

or in terms of K_d

$$K_d = \frac{K_d^0}{1 + K^0 [P]_0 C} \tag{70}$$

where C is designated the collision factor and is defined as

$$C = \frac{(1 - f)}{(e^{k'\tau} - 1)} \tag{71}$$

C is expected to be constant for a given solute/sorbent combination. Equation 69 is similar in form to Eq. 64 but has defensible thermodynamic basis.

In summary, our model assumes that (a) collisions between particles lead to energy transfer that desorbs a small fraction of solute, (b) in collisions resulting from Brownian motion, two particles will collide extensively through rotational or translational Brownian motion before they fully separate, and (c) the collision frequency is high enough to prevent conventional equilibrium from being reached. The degree of desorption in item (a) depends upon the magnitude of the volume element of the particle through which the energy is dissipated. In amorphous media, energy penetration is typically limited to a few angstroms.[120] The collision frequency in assumption (b) will depend on particle shape; e.g., rotational Brownian collisions will be absent for spherical particles. These assumptions affect the magnitude of f and τ.

Finally, we note that the model, as formulated, requires sorption to be reversible. It is well known that sorption may contain both reversible and resistant components.[125] The latter is usually associated with material diffused into the body of the sorbent. Our model applies only to the reversible component since the solute diffused into the sorbent should not be affected by local events at the particle surface.

Third-Phase Sorption

When colloidal material interferes with the two-phase distribution of an organic

solute, the general form of the measured distribution coefficient can be rewritten as

$$K_d^{apparent} = \frac{C_s}{C_w + r_{cw} C_{cw}} \quad (72)$$

Here, r_{cw} is the colloidal concentration; C_{cw} is the concentration of solute retained by the colloids; and C_s and C_w are the solute concentration in the solid and aqueous phases,respectively. By dividing through by C_w, Eq. 72 can be rewritten in terms of the "true" solid-water, K_d, and colloid-water, K_{cw}, distribution coefficients for a given pH as

$$K_d^{apparent} = \frac{K_d}{1 + r_{cw} K_{cw}} \quad (73)$$

Equation 73 can be rewritten as

$$\ln K_d^{apparent} = \ln K_d - \ln (1 + r_{cw} K_{cw}) \quad (74)$$

For measurements where the third-phase concentration is relatively low (i.e., $r_{cw}K_{cw} << 1$), the Taylor expansion of the last term in Eq. 74 and the truncation of the power series at the initial term produces a useful form in the prediction of K_{cw} values.

$$\ln K_d^{apparent} = \ln K_d - r_{cw} K_{cw} \quad (75)$$

RESULTS AND DISCUSSION

Results from a study testing the effect of fiber concentrations on the sorption of 2,4,5-TCP to kappa number 69.8 softwood fibers are listed in Table 7. The results show no measurable solids effect. Similar results were found using various mixing rates and levels of turbulence. The lack of an effect in this system can conceivably be attributed to its unique circumstances. For a pulp fiber, the lignin phase which has been shown to retain the organic sorbates is for the most part contained within the fibrous structure. This would shield it from a collisional energy transfer and a collisional desorption mechanism. It may also be argued that third-phase effects did not appear due to the minor levels of lignin macromolecules or colloidal material released by the thoroughly washed pulp fibers. Thus, the results do not counter the proposed existence of the solids effect but rather provide information on the types of systems and conditions in which it may play a role in the sorption process.

Table 7. The effect of pulp fiber concentrations on the sorption of 2,4,5-trichlorophenol to kappa number 68.9 softwood fibers.

Solids Concentration (mg/L)	K_d (mL/g)
100	68.1
500	66.0
800	68.8
1250	65.5
2500	62.6
6250	60.8
12500	62.3

Although no solids concentration effect was apparent in laboratory experiments, the enormous amount of color that exists in the bleaching effluents raises the issue of how excessive colloidal materials will impact the distribution process. Total Organic Carbon (TOC) levels measured in the filtrates of fiber sorption experiments indicate colloidal levels are low (< 5 ppm TOC), but the results also indicate these levels climb linearly with solids concentration and increase strongly with the kappa number of the fibers (Fig. 44). This is consistent with the assumption that the level of colloidal material (i.e., the third-phase concentration) increases with sorbent concentrations. For effluents from a pulp and paper mill, levels of the colloidal materials, much of which may be lignin derived, may be almost two orders of magnitude greater than that found in laboratory experiments. To determine the effect of these high levels, lignin precipitate materials were leached under high pressures (Chapter 2) to produce TOC levels in excess of 200 ppm. Dilutions of this third-phase solution were then used in sorption experiments to test Eq. 75. Figure 45 shows the sorption of both 2,4-DCP and 2,4,5-TCP to kappa number 69.8 softwood fibers as a function of the third-phase concentrations at pH of 7.00. The figure demonstrates a good linear correlation between ln K_d and the concentration of colloidal materials for the trichlorophenol as well as a somewhat less successful fit of the dichlorophenol. The resulting colloidal distribution coefficients on a colloidal mass basis, K_{cw}, calculated from the slopes of these lines, are 605 mL/g and 1405 mL/g for 2,4-dichlorophenol and 2,4,5-trichlorophenol, respectively.

The measured K_{cw} values indicate that sorption for the colloidal material is about double that for the solid lignin phase. Considering that the colloidal material will probably have several orders of magnitude more specific surface area, the results are

more consistent with a mass-based sorption process. But the mechanism of this decrease in sorption does need to be explored more thoroughly. Although the measured drop is consistent with the direct sorption of solutes by colloidal material, there is the possibility that the decrease may be caused by a more indirect mechanism. For example, the large levels of colloidal material may reduce the solute's aqueous activity coefficient or macromolecules may be competing with solutes for sorption positions. It is also important that the dependency of the colloidal effect on pH be characterized. If the colloids do retain organic solutes, it is possible that K_{cw} will have a dependency on pH similar to that of K_d (Eq. 39). The mechanism involved in the reduction of K_d is important because the colloidal material in bleaching effluents will not be settled out at the primary clarifier; therefore, if organic chemicals are truely sorbed by these suspended materials, their survival during secondary treatment, as well as their transport once released into the environment, will be strongly affected.

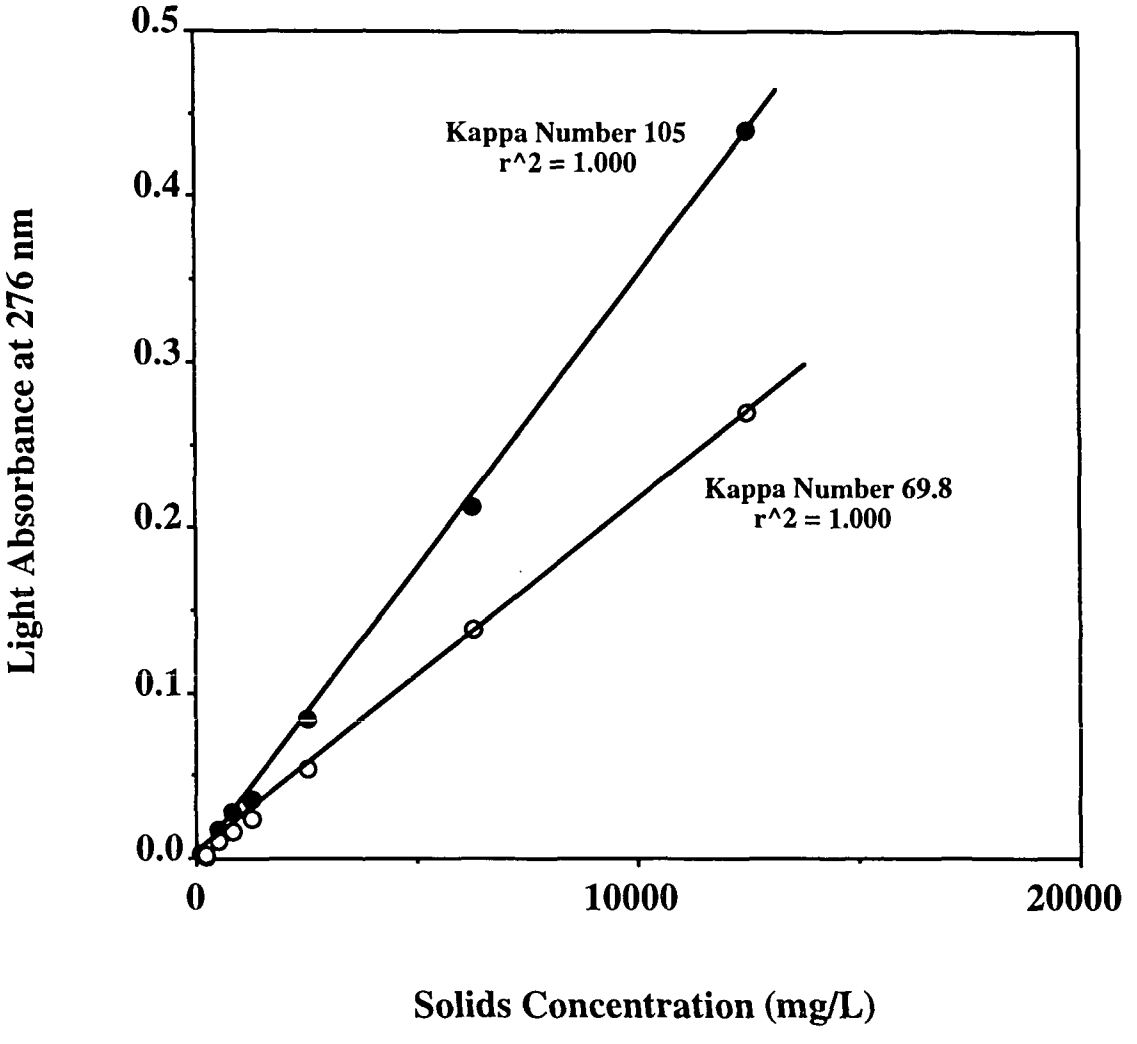


Figure 44. Increase in solution phase light absorption which is related to colloidal levels as a function of solids concentration.

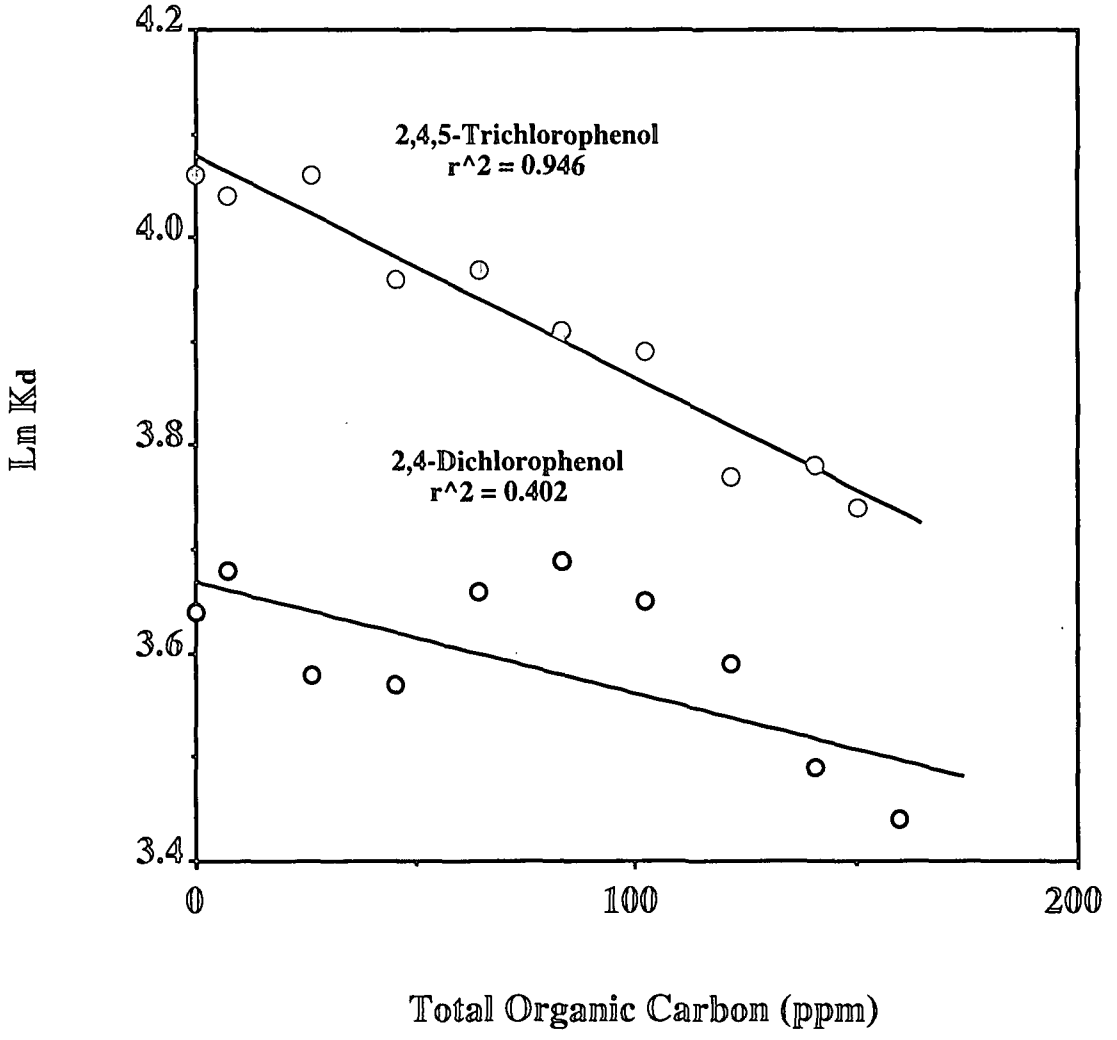


Figure 45. Sorption as a function of colloidal levels (TOC) in the aqueous phase at pH of 7.00.

CONCLUSIONS

Experiments indicate that the solids effect does not play a major role in the fiber-water distribution of chlorophenols, possibly due to the shielding of the sorbent phases from collisional energies. But the results do indicate that the presence of high concentrations of lignin-derived colloidal material does lower sorption. This may be a result of the direct sorption of solutes by colloids or other more indirect mechanisms such as a lowering of the aqueous activity coefficient of the solutes. The relatively weak dependency of K_d on colloidal concentrations allows the effect to be neglected in laboratory experiments, but the extremely high levels of colloidal materials in bleaching effluents from lignin, cellulose, and other macromolecule sources indicate that this topic needs to be explored more thoroughly under mill conditions.

SORPTION OF CHLOROPHENOLS TO PRIMARY CLARIFIER SOLIDS

INTRODUCTION

This chapter discusses the application of laboratory results in predicting the sorption of model compounds to clarifier samples. Results from sorption experiments using clarifier underflow (solid) and overflow (aqueous) were compared with predicted sorption based on the measured pH, inorganic salt concentrations, and third-phase levels of the aqueous phase and of the lignin content of the primary sludge. These measurements are meant to demonstrate how the results of this project can effectively be applied to a specific aqueous-fiber sorption process to gain both quantitative and qualitative information. The results of Chapters 1 through 5 appear to be quite adaptable to bleached kraft effluents. The suspended matter in effluents consists mainly of fibers, fiber debris, and inorganic filler and coating material such as clay, calcium carbonate, and titanium dioxide. With ample evidence that hydrophilic materials (e.g., inorganic solids) do not appreciably retain organic chemicals,[20,30–32] fiber solids should be the primary sorbents. The aqueous phase of effluents is expected to be slightly alkaline due to the heavy contribution from extractive bleaching stages. This means ionization may play a major role in determining the retention behavior of model chemicals and phenolics in general.

This chapter also reviews the results of a limited kinetics study which was run to determine a time scale for the sorption process. The study looks at the effect on sorption under "laminar mixing," which is the minimum expected in the transport of bleaching effluents to the primary clarifier. The steps involved in the sorption of

organics by a solid particle include the diffusion of the chemical from the bulk solution to the sorbent surface, the movement of the solute into the particle to locate an acceptable sorption site (in multiphase solids), and its attachment onto or partitioning into that site. For the sorption of aqueous solutes to the organic material contained within soils and sediments, uncertainty in how these chemicals are retained (e.g., adsorption or absorption) makes the modeling of this process difficult. These systems typically show a fast-slow behavior: starting out rapid, reaching 30 to 60% of equilibrium in a few minutes, and achieving final equilibrium only after a few days, weeks, even months.[126–128]

This behavior has been successfully modeled using the diffusion of solute into the solid particles (i.e., pore diffusion) as the rate-limiting step.[129–131] Here, the solute is assumed to be quickly sorbed to the outside of the solid but then must maneuver its way through an inner pore structure to find an acceptable site where it adsorbs or partitions within. In terms of this model, the observed fast-slow effect is explained as the rapid sorption of solute to easily accessible locations followed by the slow diffusion and sorption to less accessible positions. For pulp fibers, the similarity with soils and sediments (i.e., the primary sorbent, lignin, is wrapped within a composite structure composed mainly of a nonsorbing phase, cellulose) may result in similar kinetics. But, for the pulp fibers, the large passages produced during delignification are expected to present less resistance to the diffusing solutes.

RESULTS AND DISCUSSION

Kinetics

Figures 46 through 48 plot the concentration in the aqueous phase versus time for the sorption of 2,4,5-TCP by kappa number 105 softwood fibers at various solids levels. Each plot shows the data for the mixed and unmixed samples. These results demonstrate the importance of mixing in the sorption process. The mixed samples reached equilibrium in less than an hour, while the unmixed samples required several days. The mixed samples were stirred at a rate high enough to suspend the fibers, but the flow did not appear to be turbulent. For the unmixed samples, pulp was gently lowered into the aqueous phase and eventually settled to the bottom of the flask. This resulted in only a minor dispersion of the fibers and probably poor contact between the lignin phase and the aqueous solute. Under these conditions, the time required to reach equilibrium was more than three orders of magnitude greater than that required for the mixed samples. The dramatic impact of mixing on sorption was somewhat surprising. If the process is controlled by intraparticle diffusion as is typically the case in soil and sediment systems, then mixing would not be expected to have a major effect on the sorption rate. It is possible that the larger pore structure of the fibers allows for mixing in the bulk phase to impact the transport of solutes to lignin, but a much more extensive study of the sorption kinetics is necessary before any conclusions can be drawn about mechanisms.

Although the modeling of the sorption kinetics is beyond the scope of this study, the results do provide insight on the applicability of K_d values in predicting sludge retention of organics. It appears that even under limited mixing conditions, the

sorption of 2,4,5-TCP achieves equilibrium rapidly (i.e., in less than an hour). Based on these results, it is expected that the countercurrent flow through the bleaching towers and the pumping of bleaching effluents to the primary clarifier will provide ample time for the system to near or achieve an equilibrium distribution of organic chemicals between the aqueous and solid phases.

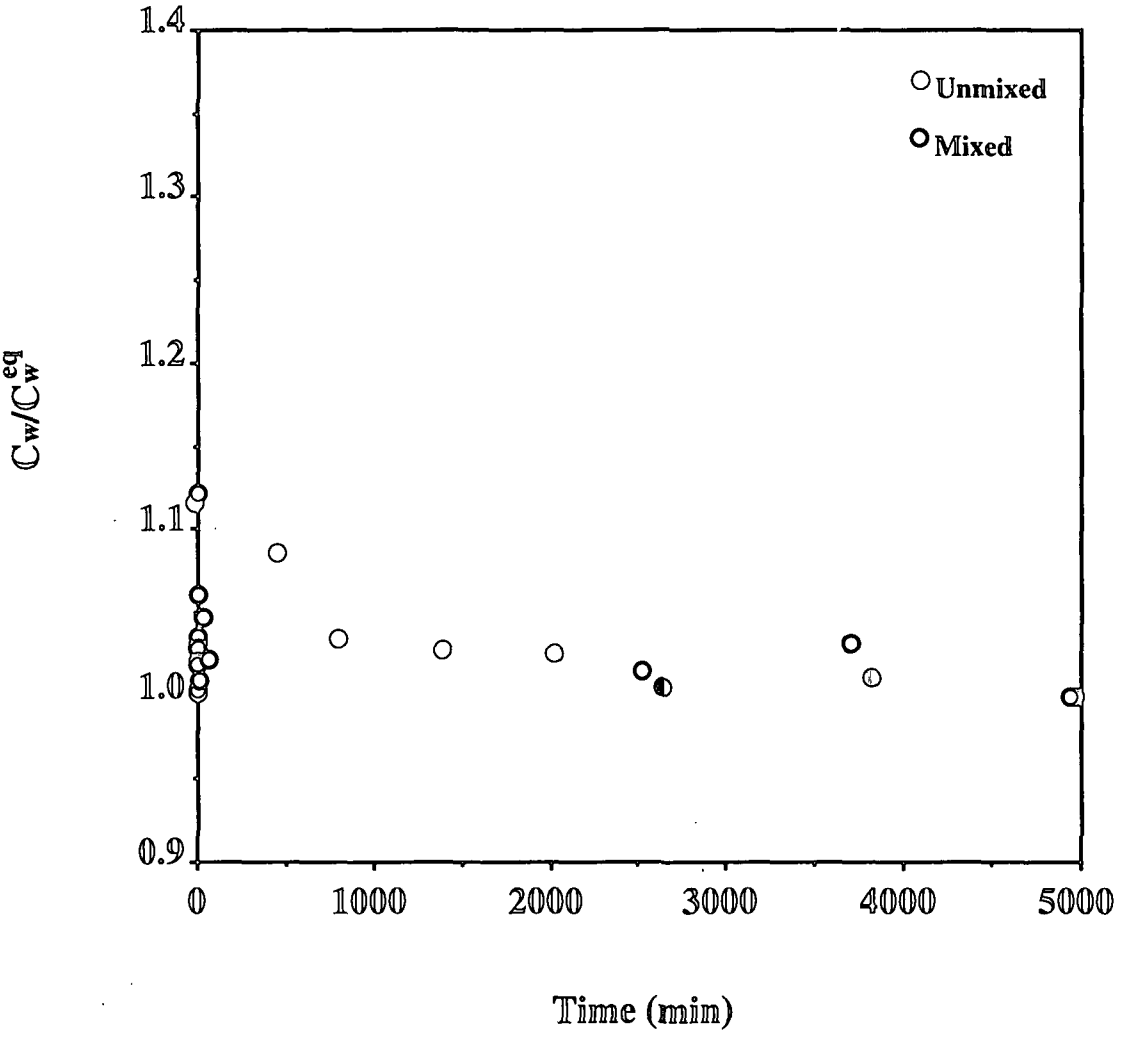


Figure 46. Sorption of 2,4,5-trichlorophenol to kappa number 105 softwood fibers (1000 mg/L) at pH of 7.00.

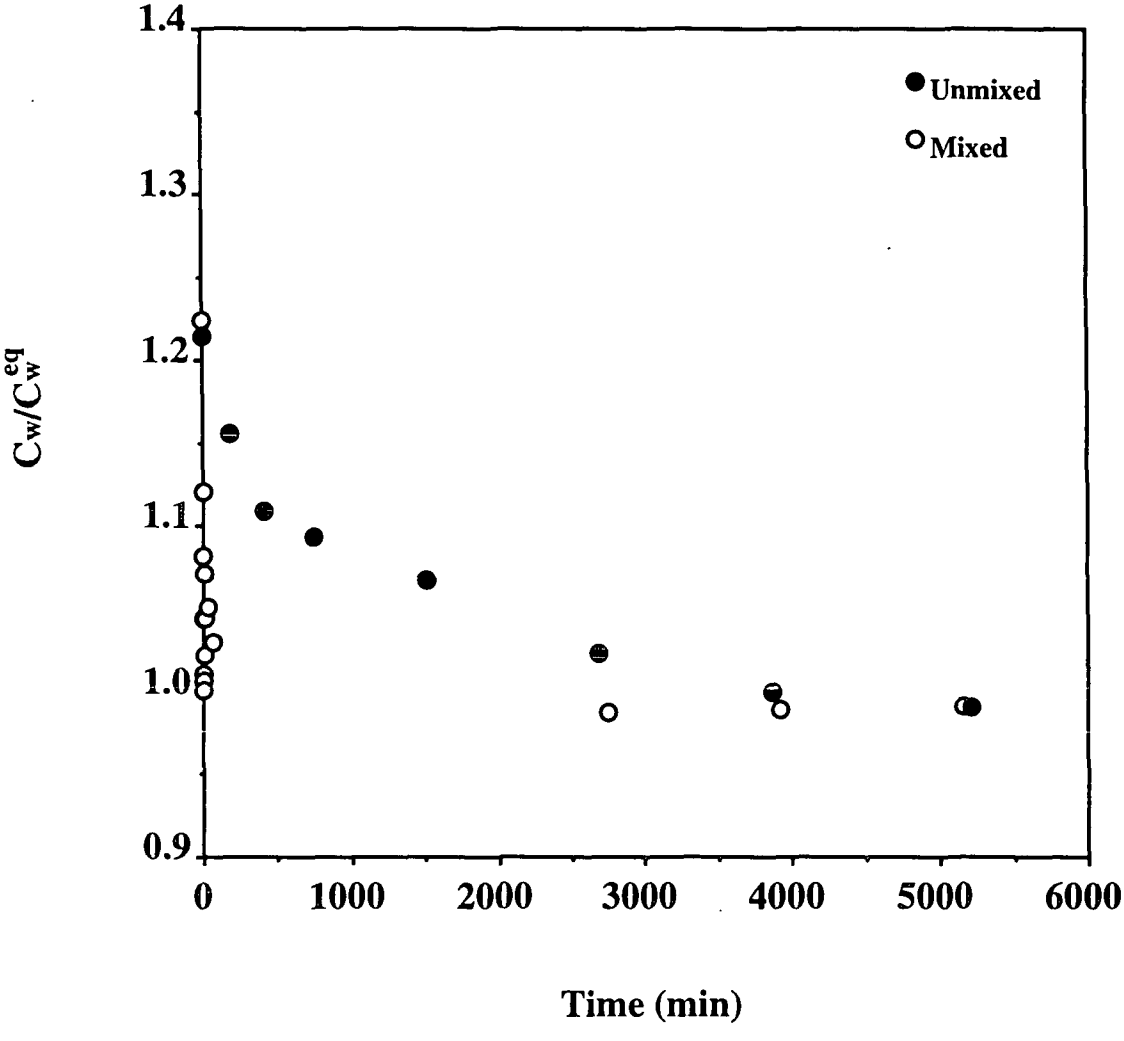


Figure 47. Sorption of 2,4,5-trichlorophenol to kappa number 105 softwood fibers (2000 mg/L) at pH of 7.00.

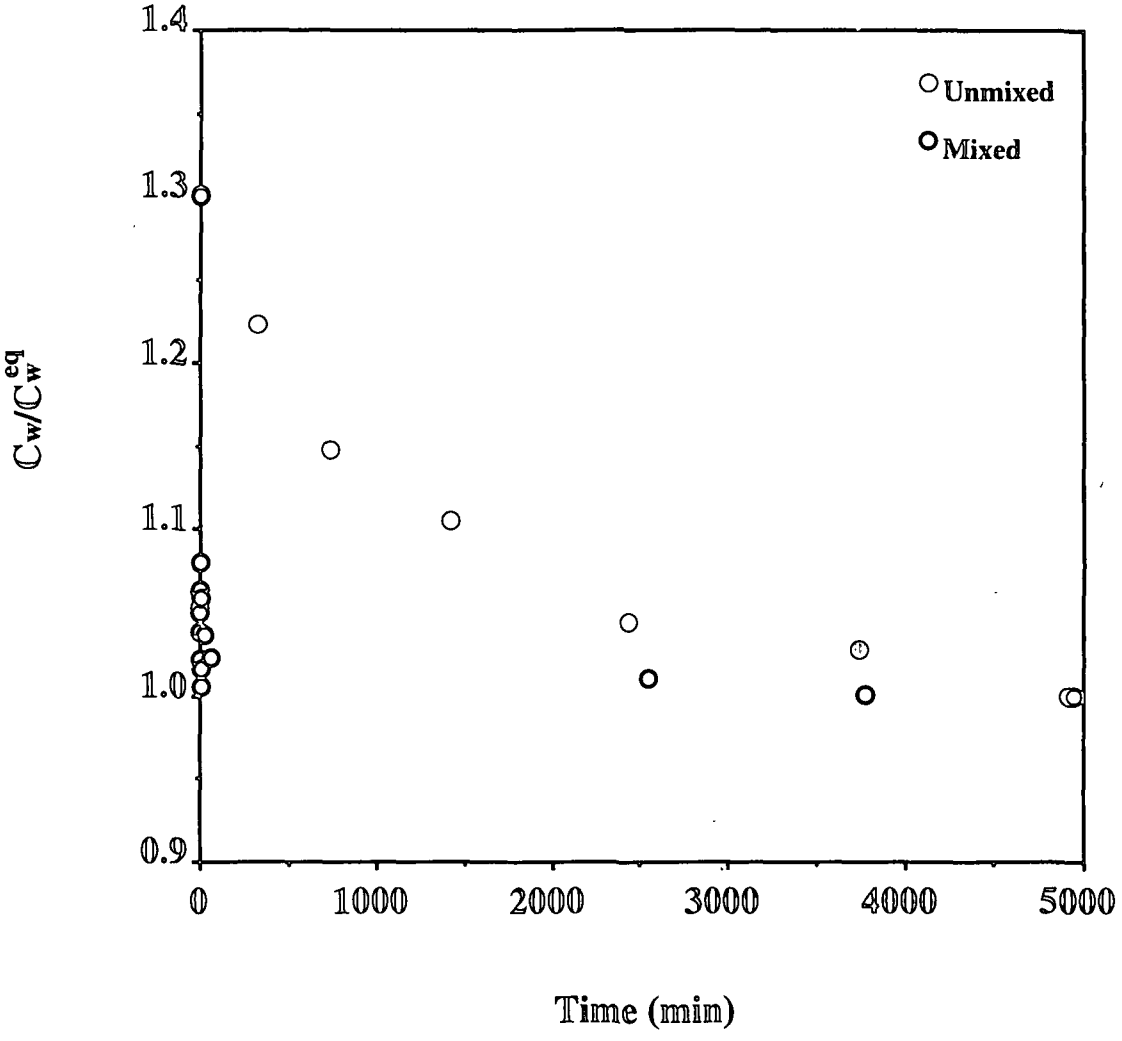


Figure 48. Sorption of 2,4,5-trichlorophenol to kappa number 105 softwood fibers (3000 mg/L) at pH of 7.00.

K_d Measurements

The measured properties of the solid and aqueous phases from the primary clarifier samples are summarized in Tables 8 and 9, respectively. Sludge can contain a variety of inorganic and organic components, but it is expected to be primarily composed of fiber-derived solids and inorganics such as lime and clay. Combustion at 525°C and 900°C indicates a relatively high level of ash. The difference between ash levels measured at the different temperatures indicates a strong presence of $CaCO_3$ which decomposes at around 800°C to form solid CaO and CO_2 gas. For the lignin content, an acid-insoluble lignin test with a lignin ash correction (i.e., combustion at both 525°C) were used to make an estimate. Estimates of the lignin content of primary sludge are difficult to obtain. The sludge is highly nonhomogeneous which may result in dramatic composition variations in samples, and the combination of non- and highly oxidized lignin and the presence of other organic materials makes the use of a standard lignin content test for sludge a questionable measure. Acid insoluble levels in the sludge without shives were about 8%, but the actual lignin levels are expected to be greater due to contributions from more highly oxidized lignin sources that are probably not accounted for in the test and the shives which were not measured.

Table 8. Primary sludge characteristics on oven-dried mass basis.

	% mass
Ash levels measured at 545°C	22.8
Ash levels measured at 900°C	14.8
Acid Insoluble Solids Corrected for Ash	7.89

Table 9. Clarifier overflow characteristics.

Total Organic Carbon (TOC)	410ppm
pH	7.77
Chloride	740ppm
Sulfate	740ppm
Fluoride	0.38ppm
Nitrate	0.017ppm
Phosphorus	3.4ppm

In the aqueous phase, the inorganic salt concentrations appear to be quite low. Results from the sorption of model chemicals to pulp fibers indicate that a KCl concentration of about 10,000 ppm is necessary to produce a 5% change in fiber-water K_d values. Although each inorganic salt has its own impact on sorption, with some even causing a salting-in effect, salts typically have a positive Setchenow constant of between 0.2 and 0.4.[91] The sum of all ions which were measured in this study indicates a low salt concentration (< 1500 ppm). At these levels, it is expected that the effect of inorganic salt on the retention of organic chemicals by clarifier solids can be neglected. Colloidal concentrations, on the other hand, are very high. If all the colloidal phase is completely lignin-derived, a drop in K_d of as much as 14% for 2,4-DCP and 27% for 2,4,5-TCP is expected (Eq. 74), but it is difficult to determine how much of this material is lignin-derived and how much is derived from other more hydrophilic organic sources which would not produce a strong third-phase effect.

Table 10 shows the measured distribution of the model compounds between a pH 7.00 aqueous buffer and the various components of clarifier solids. Table 11 lists the

measured K_d values for the distribution of the model chemicals between the collected sludge and clarifier overflow phases. The results indicate, again, the role of ionization and lignin in the sorption process. The materials that are expected to contain high levels of lignin have high K_d values. FTIR analysis of the fines indicated that lignin and carbohydrates were present at high concentrations. It also indicated the possible presence of other material such as bark. The sorption by this "fiber debris" is about half of what was measured for the lignin precipitates (Chapter 3), which is consistent with a high concentration of more hydrophobic materials such as lignin. This material is found throughout the sludge and coats the fibrous materials. Washing the fibrous components with a pH 9.00 buffer partially removed the debris and dropped sorption by more than 50%, indicating that the fines are the primary substrate for chlorophenol sorption in the unwashed fibers.

Table 10. The distribution of model compounds between sludge and sludge components and distilled water at a pH of 7.00.*

	K_d (mL/g)	
	2,4-dichlorophenol	2,4,5-trichlorophenol
Whole Sludge	68.6 ± 12.1	112 ± 20
Shives	101 ± 6	146 ± 5
Unwashed Fibers, Shives Removed	61.7 ± 8.3	101 ± 11
Washed Fibers, Shives Removed	28.4 ± 6.0	43.4 ± 4.4
Fines	201 ± 6	331 ± 7

* except for the fines which were run in the clarifier overflow solution at an adjusted pH of 7.00.

Table 11. Predicted and measured results for the distribution of model compounds between primary sludge and clarifier overflow solution at a pH of 7.77.

	K_d^{meas} (mL/g)	K_d^{pred} (mL/g)*
2,4-dichlorophenol	40.6 ± 6.1	43.6
2,4,5-trichlorophenol	33.1 ± 5.7	29.9

* based in sorption measured in pH 7.00 buffer (see text)

The drop in sorption which accompanies the move from an aqueous pH 7.00 buffer and the clarifier overflow at pH of 7.77 is consistent with the predicted dominance in the sorption process of the neutral form of the model chemicals. In fact, using Eq. 42, $f_l K_l^0$ values estimated from the sorption to whole sludge of model compounds from the aqueous buffer accurately predict sorption to sludge from clarifier overflow (Table 11). This result indicates that under mill conditions, inorganic salt and colloidal concentrations had little impact on sorption. The lignin level in sludge estimated from sorption values is about 20%. This is more than twice the level measured using the acid insoluble lignin test. These tests were run without the shives, but their presence would not make up this difference. Earlier in Chapter 3, it was shown that an acid insoluble test on the bleached fibers measured a lignin concentration which was about half of that indicated by the sorption of model compounds. It is likely the material collected from the clarifier will have a similar oxidation level, which may account for the low estimate of the amount of lignin capable of retaining the chlorophenols.

If it is assumed the primary sludge contains a 20% lignin, the fiber-solids are responsible for a majority of the sorption of organic chemicals, and that the results

for sorption of chlorophenols applies to other chlorophenolic chemicals, predictions for the sorption of other chlorophenolic chemicals can be made using Eq. 42 and the chemical's pK_a and $\log K_{ow}$ values.[1,132] Table 12 lists $\log K_{ow}$, pK_a, and sludge-water K_d values for the model compounds and general ranges for several other phenolic molecules which are found in bleaching effluents. Although these chemicals have a broad range of hydrophobicities (as measured by $\log K_{ow}$), the predicted K_d values have a very small range of between about 1 and 60 mL/g. This appears to be the result of a balance between increased hydrophobicity and ionization which accompanies increased phenolic chlorination. Chlorine atoms increase the size of a compound without significantly increasing its polarity and, thus, increase their hydrophobicity. But for chlorophenolic chemicals, the chlorine atoms will stabilize the ionized form of the compound. Therefore, increased chlorination promotes ionization (i.e., lowers pK_a values). Thus, the increased presence of chlorine atoms has the opposing effects of raising the hydrophobicity of its neutral form while decreasing the compound's overall hydrophobicity through ionization. This translates into low sorption values for the chlorinated phenolic chemicals. It is interesting to note, however, that, in the absence of ionization, the predicted sorption of these compounds would be very high. For example, the K_d predicted for 2,4,5-trichlorophenol at the clarifier if it were not ionized would be close to 300 mL/gm.

Table 12. Log K_{ow} and pK_a values for model compounds and ranges for several chlorinated phenolic compounds.

Compound	log K_{ow}	pK_a	K_d (mL/g)
2,4-Dichlorophenol	3.20†	7.87‡	41.0
2,4,5-Trichlorophenol	3.72†	6.92‡	33.1
6-Chlorovanillin	1.5 ~ 2.0	7.5 ~ 8.6	0.614 ~ 4.58
5-Chlorovanillin			
2-Chlorosyringaldehyde			
4,5-Dichlorocatechol	2.2 ~ 2.7	7.0 ~ 8.6	1.18 ~ 21.2
3.4-Dichloroguaiacol			
4,5-Dichloroguaiacol			
5,6-Dichlorovanillin			
2,6-Dichlorosyringaldehyde			
2,4,6-Trichlorophenol	3.0 ~ 3.5	7.0 ~ 7.75	6.78 ~ 67.6
3,4,5-Trichlorocatechol			
3,4,5-Trichloroguaiacol			
4,5,6-Trichloroguaiacol			
Trichlorosyringol			
Tetrachlorocatechol	3.7 ~ 4.0	6.0 ~ 7.0	3.62 ~ 60.6

† log K_{ow} for model compounds are experimental values.
‡ pK_a for model compounds are measured values.
The ranges are based on both available experimental and predicted values.[132]

CONCLUSIONS

In summary, kinetic studies indicate that under gentle mixing conditions (i.e., magnetic stir-rod at rates just sufficient to suspend the fibers) the sorption process achieves equilibrium in a matter of minutes, indicating distribution coefficients are an accurate means of describing the distribution of chloro-organic chemicals in bleaching effluents. K_d measurements show lignin to be the dominant carrier of residual organic compounds from pulping and bleaching operations. For collected whole sludge samples, the lignin retention translated into chlorophenolic sludge concentrations which are about an order of magnitude above that in the clarifier overflow waters at a pH of 7.77. Phenolic sorption appears to be controlled by the compound's hydrophobicity which increases with chlorination and dramatically falls with ionization. With the effluents which pass through the clarifier typically coming from extractive bleaching stages, the aqueous phases are mainly alkaline, and the retention of chlorinated phenolics is expected to be small, but for organic structures that do not contain an ionizable acid group, sorption unrestricted by ionization will climb strongly with the compound's hydrophobicity. Estimates of the sludge-water distribution of neutral compounds indicate that sludge concentrations can climb to many orders of magnitude above their levels in the bleaching influents.

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS FOR FUTURE WORK

The goal of this project was to develop "engineering" type equations for predicting the equilibrium sorption of aqueous organic solutes to pulp fibers and fiber-derived solids and in the process develop a greater understanding of this distribution mechanism. This project was successful in its goals for the model chemicals (i.e., 2,4-DCP and 2,4,5-TCP) which are representative of many of the moderately hydrophobic materials found in bleaching effluents. With respect to concentration, experiments showed that isotherms could be fit with a linear model within the concentration region common to the chloro-organics found in bleaching effluents. This allows equilibrium sorption to be described by a single term (i.e., independent of solute concentration), the fiber-water distribution coefficient, K_d. Isotherm studies using chlorophenols and chlorophenol mixtures at relatively high concentrations (> 7 ppm) indicate that sorption is also independent of organic cosolute concentrations, and measurements of sorption to ground fibers showed that increased surface area had no impact on the process.

The results of kinetic measurements were supportive of an equilibrium model for the distribution of chloro-organics during wastewater treatment with mixed samples reaching equilibrium in a matter of minutes. It was also shown that the sorption of model chemicals by pulp fibers was limited to the retention of the acid form of these compounds to the lignin fraction of the fibers. This led to the development of an equation which relates the overall fiber-water distribution coefficient, K_d, to the fraction of the compound in the neutral or acid form, α, the mass fraction of lignin in the fibers, f_l, and the lignin-water distribution coefficient for the neutral chemical,

K_l^0

$$K_d = k_w + 0.0015\,\eta\,\alpha\,K_l^0 \approx \alpha\,f_l\,K_l^0 \qquad (42)$$

which can be estimated with a linear free-energy relationship. A thermodynamically consistent model was developed for a collisional desorption-induced solids effect, but the fiber system did not demonstrate a sorption dependency on sorbent concentration. Lignin-derived colloidal material was shown to lower sorption which could be modeled with an equation which assumes sorption by colloidal material. The effect from inorganic salts and temperature was successfully modeled by treating the sorption of model chemicals as a phase distribution between water and lignin phases, but both effects were small and are not expected to impact sorption under mill conditions.

To test the application of these results under mill conditions, the sorption of model chemicals to overflow and underflow samples collected from the primary clarifier at a bleached kraft mill were measured. The results were consistent with the fiber-water system, and application of developed equations indicate chlorophenolic chemicals will have a low retention by effluent solids due mainly to ionization, but nonpolar neutral organics may concentrate in the lignin components of primary sludge to many levels above their solution phase concentrations.

In general, the results of this project demonstrate that hydrophobic interactions may play a much greater role in the retention of organic materials by fibers than previously believed. Even with the ability to hydrogen bond to cellulose, the sorption of the moderately hydrophobic model chemicals and the effect of variables such as

temperature and ionic strength were modeled solely on the basis of their aversion to water. Based on this result, it is reasonable to believe that hydrophobic interactions may dominate other processes where an organic chemical is retained by fibrous solids such as contaminant retention by recycled fibers and the sizing of paper. The application of results from this project to these types of processes appears to be a natural extension of this work. From an environmental standpoint, the greatest benefit from future research would come from a study on retention of chloro-organics by suspended effluent solids. It is possible that sorption to materials such as colloids, lignin precipitates, and biomass may collect adsorbable organic halides (AOX) components and impede biological treatment. By modeling the interaction between these chemicals and suspended solids and determining how sorption impacts the treatment process, a greater understanding of the transport and fate of bleaching effluent chemicals can be developed which may change the way the paper industry treats its effluents.

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